Route to Attosecond Nonlinear Spectroscopy

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We demonstrate generation of coherent microjoule-scale, low-order harmonic supercontinua in the deep and vacuum ultraviolet (4–9 eV), resulting from the nonlinear transformations of near-single-cycle laser pulses in a gas cell. We show theoretically that their formation is connected to a novel nonlinear regime, holding promise for the generation of powerful deep-UV and vacuum ultraviolet subfemtosecond pulses. Our work opens the route to pump-probe spectroscopy of subfemtosecond-scale valence-shell phenomena in atoms, molecules, and condensed matter.

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Isolated attosecond pulses in the extreme ultraviolet (XUV) emerge as a result of the interaction of intense ionizing laser fields with atoms [1]. The extreme nonlinearity of this interaction along with a variation of the driver field amplitude and direction over the wave cycle allows the resultant XUV emission to be confined to a fraction of the laser-field cycle. In all approaches that have permitted demonstration of attosecond pulses to date [2–5], the controlled formation of several-electronvolt-broad spectral supercontinua has constituted the most critical prerequisite for the subfemtosecond temporal confinement of the emerging radiation. Access to and control of the spectral phase of these supercontinua—currently available in the range of 20–120 eV—completed these technologies [6,7], which are now the sustaining pillars of modern attosecond experiments [7–9].

Extension of attosecond sources to the deep and vacuum ultraviolet (4–9 eV) will open up new prospects in attosecond science. It will allow subfemtosecond site-selective resonant excitation of manifolds of valence electronic states to create rapidly evolving electronic wave packets in molecular orbitals [10]. Steering of these wave packets with controlled laser fields [11,12] may open new avenues towards controlling chemical reactions [13].

Subfemtosecond pulse generation in the deep and vacuum ultraviolet calls for both conceptual and technical advancement. To date, the shortest UV pulses have been generated via direct third-harmonic generation by few-cycle near-infrared (NIR) pulses [14], yielding pulses with durations of 3.7 fs [15] and more recently of 2.8 fs [16]. However, due to the moderate nonlinearity of low-order harmonic conversion the generation of subfemtosecond pulses via this process is hardly feasible even with single-cycle IR driver pulses. We show in this Letter that spatiotemporal nonlinear transformations of a near-single-cycle NIR pulse in a pressurized quasistatic gas cell constitute a promising approach towards breaking the 1 fs barrier in the UV spectral range.

Exploitation of macroscopic spatiotemporal transformations of a light pulse in a nonlinear medium for the control of its spectral content, duration and power has become a rapidly developing research area in ultrafast optics [17–19]. The propagation in filaments has been shown to be useful for pulse compression [20,21], as well as for providing ideal conditions for efficient third-harmonic generation [22–24] and compression of UV pulses to pulse widths below 2 fs inside the filament [25]. Here, we show both theoretically as well as experimentally that filamentation nonlinear optics implemented with powerful near-single-cycle light pulses [26,27] offers a conceptually new short-pulse generation strategy permitting the production of subfemtosecond pulses in the UV-VUV (4–9 eV) with unprecedented peak power.

To model the spatiotemporal dynamics of high-intensity ultrashort waveforms in a fast-ionizing gas medium, we numerically solve the evolution equation for the electric field with a standard set of assumptions in the framework of the slowly evolving wave approximation [28] (see, e.g., Refs. [29,30] for a detailed description of the model). Briefly, dispersion of the gas medium enters into our model through the frequency profile of the wave number $k = k(\omega)$, which automatically includes high-order dispersion effects. Beyond the dispersion of the atomic gas, this equation accounts for all other phenomena affecting the evolution of an ultrashort pulse in an ionizing medium, such as plasma dispersion, beam diffraction, spatial and temporal self-action of the laser field induced by the Kerr effect, ionization, and fifth-order atomic optical nonlinearity.

The dynamics of the electron density n_e is included in the model through the equation $\partial n_e/\partial t = w(n_0 - n_e)$, with n_0 being the density of neutral species and w being the ionization rate, calculated by using Keldysh-type equations (see, e.g., Refs. [17,18] for details).

For our simulations we have considered intense (300 μJ) near-single-cycle pulses ($\tau_p = 3.3$ fs) centered around 750 nm and focused ($f = 60$ cm) into a well-confined ensemble of neon atoms in a quasistatic cell (3 mm) at densities of 2×10^{20} atoms/cm^3 at a backing pressure of $p_0 = 9$ bar. The gas-pressure profile across the quasistatic gas cell is modeled as $p(z) = p_0 \exp[-(z/\zeta)^{10}]$, with $\zeta = 1.35$ mm. The peak intensity was $I = 10^{14}$ W/cm^3. All parameters have been chosen so as to match those of the experiments presented in the next paragraphs. Although our calculations model the complete spectral dynamics during propagation, in this Letter we focus our efforts and presentation on the nearly unexplored range of UV and vacuum ultraviolet (VUV), 300–120 nm, where the experiments presented in the next paragraphs provide direct comparison. Spectral broadening by Kerr-effect-induced self-phase modulation as well as strong blueshifting caused by self-steepening of the pulse envelope and ultrafast electron density buildup [21] are found to be the two key mechanisms in the interaction under consideration. These two blueshifting mechanisms transfer approximately 10% of the input pulse energy to the 400–600 nm wavelength region within the above-specified interaction length. The efficiency of energy conversion due to ionization-induced blue shifting [17,18,29] is approximately a factor of 2 higher than that resulting from self-steepening. Furthermore, in this regime the UV part of the spectrum is strongly enhanced by the third-harmonic generation [Figs. 1(a)–1(c)] due to the atomic third-order susceptibility $\chi^{(3)}$. Moreover, the third-order optical nonlinearity during propagation broadens the spectrum [Figs. 1(b) and 1(c)] of the emerging third harmonic via the self-phase modulation of the pump and cascaded four-wave mixing. This latter process involves the spectrally broadened visible part of the field and its UV components produced through third-harmonic generation, resulting in the formation of a UV and VUV supercontinuum.

Figures 1(d)–1(f) illustrate the spatial dynamics of the propagation and the associated spatiotemporal transformations of the laser pulse inside the quasistatic gas cell sampled at characteristic locations along the focus indicated in Figs. 1(a)–1(c). The most notable effect is the gradual defocusing of the pulse's trailing edge, the intensity of which is hence considerably reduced. The strong negative lens causing this defocusing is due to the steep ionization profile (~ 2 fs) that the driver pulse creates during its propagation in the pressurized gas medium. This ultrafast ionization-assisted self-defocusing of the trailing edge of the driver pulse tightly confines all the nonlinear processes described above to the leading edge of the driver pulse, where the driver field intensity is high.

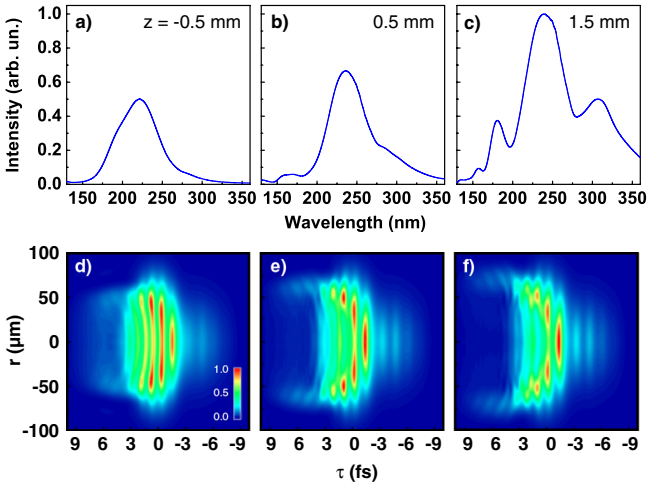

FIG. 1 (color online). (a–c) Dynamic evolution of the UV part of the supercontinuum generated by a near-single-cycle pulse, at different propagation distances along a quasistatic cell filled with pressurized neon. (d–f) Near-field spatiotemporal profiles of the propagated pulse along positions in the focus, according to (a–c).

Figures 2(a) and 2(b) compare the far-field spatiotemporal profiles of the entire laser pulses and the UV pulses (130–300 nm) filtered off the emerging supercontinuum at a distance of 1 m downstream the quasistatic cell. This comparison clearly visualizes the tight confinement of UV-supercontinuum generation on the leading edge of the laser pulse. As shown in Fig. 2(c), this confinement yields 950-attosecond UV pulses on the beam axis. The spectrum of the UV supercontinuum generated under these conditions [Fig. 2(d)] has a spectral width (FWHM) of ~ 2 eVand extends over the range 4–9 eV. Its transform-limited pulse duration (FWHM) was evaluated to be ~ 800 attoseconds. The spectral filter applied to select the UV part of the supercontinuum in simulations presented in Fig. 2(d) is based on the spectral response of the optical elements that are used in the experiments. The UV supercontinuum is dominated by a high-intensity peak around 5 eV from direct $\chi^{(3)}$-induced third-harmonic generation. The fifth-order atomic susceptibility $\chi^{(5)}$ gives rise to fifth-harmonic generation, which, however, can be isolated in the output spectra only for relatively long light pulses (> 5 fs) [31] and low gas pressures. For near-single-cycle laser pulses interacting with a high-pressure gas, direct $\chi^{(5)}$-induced fifth-harmonic generation is completely masked by cascaded four-wave mixing processes. In this regime, the third and fifth harmonic are no longer observed as isolated features but contribute to an extended UV wing of the supercontinuum spectrum. Modulation of this UV wing by cascading four-wave-mixing processes [Fig. 2(d)] translates into a noticeable modulation of the temporal pulse envelope [Figs. 1 and 2(a)]. The calculated energy of the UV pulse behind this filter is 160 nJ.

To further investigate the role of ionization-induced defocusing in the generation of subfemtosecond pulses in the UV, we have numerically switched off ionization

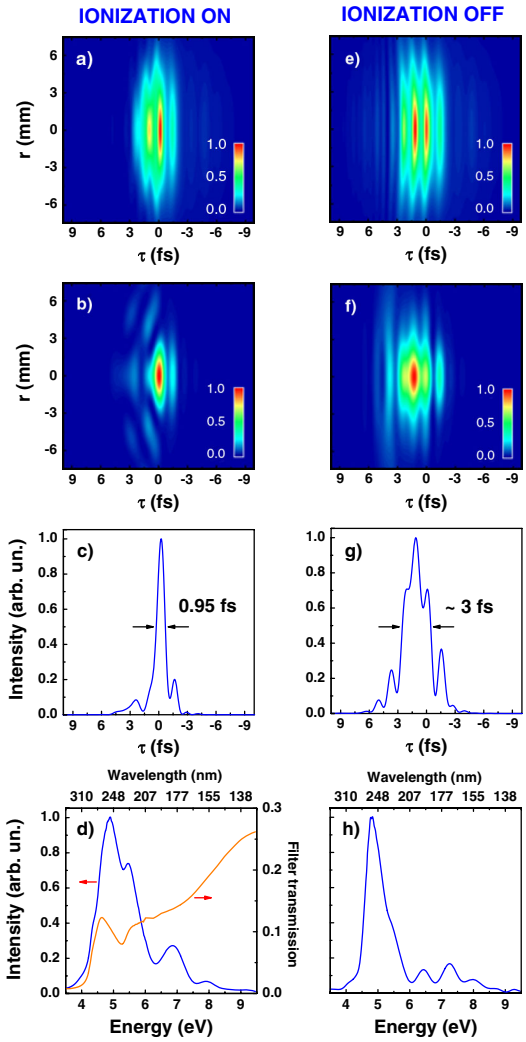

FIG. 2 (color online). Calculated far-field spatiotemporal structure of the driving pulse and the generated UV with (a),(b) and without (e),(f) ionization-induced defocusing. The FWHM temporal durations of the UV pulses are ~950 as in the case where ionization is on (c) and ~3 fs if ionization is off (g). Spectra of the generated pulse after the filtering are depicted in (d) and (h), together with the filter function in (d). Ionization-induced optical nonlinearities yield a supercontinuum in the UV and VUV (d).

but have kept all the other nonlinearities active [Figs. 2(e)–2(h)]. It is remarkable that the temporal intensity profile of the filtered UV radiation now fills a much broader temporal window of ~3 fs [Fig. 2(g)], comparable to the duration of the driver pulse. With ionization switched off, ionization-induced blueshifting is also suppressed leading to a substantially narrower spectrum of the filtered UV radiation [Fig. 2(h)], thus limiting the potential for pulse compression.

In strong contrast to previously demonstrated schemes [29,32], the near-single-cycle-driven nonlinear transformations deliver ultraviolet pulses in the far-field that are nearly free of spatial chirp, as revealed by Fig. 2(b). Spatial integration over the entire beam profile results in less than 20% broadening with respect to the on-axis

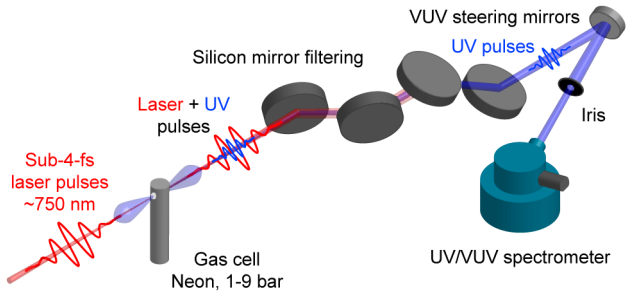

FIG. 3 (color online). Generation and measurement of UV and VUV supercontinua.

temporal profile. These characteristics are particularly important in spectroscopic applications.

To seek experimental evidence for the existence of this novel nonlinear regime, we have focused ($f = 600$ mm) near-single-cycle NIR pulses [26,27] into a quasistatic neon cell (inner diameter ~3 mm), placed in a vacuum chamber [Fig. 3]. The pressure of neon was varied in the range of 1–9 bar, while the background pressure was lower than ~2 mbar. The emerging UV pulses are isolated from the intense fundamental beam by a module comprising two pairs of silicon mirrors, located ~1 m downstream the generation cell. The first pair is oriented at Brewster's angle (~ 74°) of the p-polarized fundamental (~ 750 nm) [15], while the second pair is oriented at Brewster's angle of the beam's s-polarized component which—due to the imperfect contrast ($s{:}p \sim 10^{-3}$)—is still considerable and could hinder the temporal characterization of UV pulses [16]. A couple of VUV optimized mirrors are used to steer the UV beam (diameter ~1.3 cm) to an intensity-calibrated spectrometer. The overall optical system transmission is shown in Fig. 2(d). The energy of the pulses was measured with a photodiode-based energy meter (200–300 nm).

Figure 4 summarizes the experimental results. UV spectra that are generated with longer (~ 6 fs) driver pulses are shown in Fig. 4(a). The discrete 3rd and 5th harmonic lines appearing are in good agreement with the prediction of our simulations as well as with the results of previous experiments performed with quasimonochromatic excitation [31]. Spectra recorded with sub-4 fs pulses for a range of neon gas pressures in the quasistatic cell are shown in Fig. 4(b)–4(d) along with the energy of the UV pulses at the spectrometer. In Panels (a) genuine harmonics, (b) maximum yield with single-cycle driver, and (d) broadest spectrum with single-cycle driver, we contrast our measurements (solid lines) with the results of the numerical simulations (dashed lines) and find good agreement. In accordance with the spectral broadening scenario outlined above, higher gas pressures assist in generating broader spectra stretching further into the UV region. At $p_0 = 9$ bar, the measured [solid line in Fig. 4(d)] as well as the simulated spectra [dashed line in Fig. 4(d)] permit, in principle, bandwidth-limited pulses down to ~800 as, while the simulation suggests slightly longer pulses ~950 as. The dramatic difference between the UV spectra generated with 6 fs and sub-4 fs driver pulses

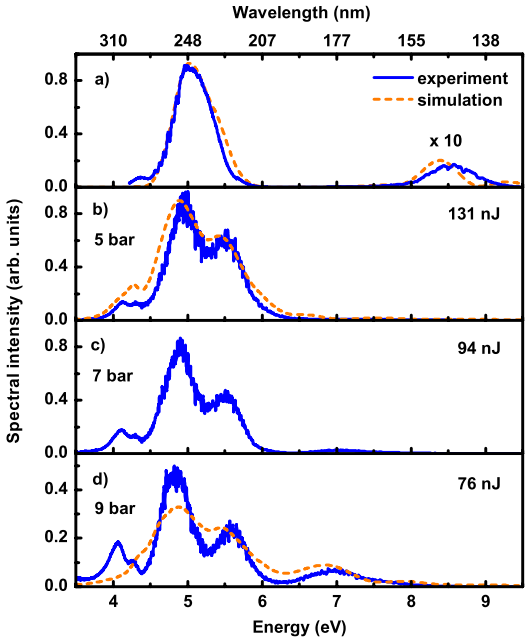

FIG. 4 (color online). UV and VUV supercontinuum generation in the few and near-single-cycle regime. Third and fifth harmonic spectra (a) generated with ~6 fs pulses at 5 bar and supercontinua generated with sub-4 fs pulses at 5 bar (b), 7 bar (c), and 9 bar (d) of neon [solid (blue) line], are plotted together with the results of the numerical calculations [dashed (orange) line] and measured pulse energies after the filtering. The bandwidth-limited durations are about 2.6 fs (a), 1.2 fs (b), 1.1 fs (c), and 0.8 fs (d).

under otherwise identical experimental conditions [see Figs. 4(a) and 4(b)] corroborates our claim about a new regime of spatiotemporal nonlinear light-matter interactions based on (near-)single-cycle driver light.

Measurements of the energy of the pulses are indicated for each backing pressure in Fig. 4. The transmission function of our silicon mirror module allows the estimation of 1.5–2 μJ at the source (corresponding to $\sim 10^{12}$ photons/s), which is slightly higher compared to previous measurements [15]. The broadest supercontinuum ($p_0 = 9$ bar) carries ~40% lower energy than the maximum pulse energy, measured at $p_0 = 5$ bar.

In summary, we have investigated a novel regime of nonlinear interactions where spatiotemporal transformation of the near-single-cycle in gaseous media is particularly favorable and offers a new route for the efficient generation of subfemtosecond pulses in the deep and vacuum ultraviolet. This regime results in the generation of intense supercontinua of UV and VUV light, the broadest and most intense supercontinua generated in this spectal range to date. Although we have employed sub-4 fs pulses in our experiments, the simulations suggest that pulses ~4 fs could be short enough to generate near-1 fs UV and VUV pulses, with noncompromised photon flux and beam quality. Our simulations predict a near-transform-limited temporal structure, suggesting the emergence of subfemtosecond, gigawatt-peak-power UV and VUV pulses from the interaction. The demonstrated source therefore holds promise for combining subfemtosecond temporal resolution with intensity levels in the range of 10^{14} W/cm^2. These pulses are also intense enough to be used as a pump in combination with a weak attosecond (XUV) probe, opening the door to studying a wide range of electron dynamics in the valence shell of molecules and solids.

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