

Vacuum ultraviolet pulses of 11 fs from fifth-harmonic generation of a Ti:sapphire laser

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We demonstrate that in a short Ar cell, generation of the fifth harmonic from 12 fs pulses at 810 nm directly results in ultrashort vacuum UV pulses at 162 nm. They have a spectral width of ~ 5 nm and a duration of 11 ± 1 fs (1.4 times the transform limit), as measured by cross correlation with the fundamental pulses. Their energy (estimated to 4 nJ) turned out to be sufficient for use as a pump in time-resolved experiments.

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It is nowadays common to produce few-cycle pulses at the fundamental (≈ 800 nm, period 2.7 fs) of the Ti:sapphire laser, and high harmonics with durations below 1 fs can be generated from them (see, e.g., [1]). However, time-resolved spectroscopy of molecules usually requires pump pulses in the near UV to vacuum UV (VUV). In this spectral region, such a short pulse duration is not yet standard, and this lack has limited the time resolution in many pump-probe experiments. Recently we demonstrated [2] that sub-10-fs pulses at 270 nm can be simply generated by frequency tripling in a short Ar cell. (The same communication also reported on tunable 10 fs UV pulses from supercontinuum generation in longer Ar cells.) It was argued that the previous methods are much more complicated and challenging. We also suggested that further shortening should be feasible by shortening the fundamental with the known techniques. This possibility has in the meantime been shown at 270 nm by Goulielmakis and Graf [3]. In the VUV, where many small molecules have their first absorption band, generation of short pulses has been considered to be more difficult because of the refractive index dispersion of transmissive optical materials including gases. At 155 nm, pulse durations of 300–450 fs were previously obtained by near-resonant four-wave difference-frequency mixing in Ar [4,5] and recently 160 fs by nonresonant four-wave difference-frequency mixing in Ar-filled hollow metalized quartz glass fibers [6]. It has also been demonstrated that pulse durations of 13 fs can be obtained by compression of negatively chirped 160 nm pulses [7]. In this Letter we extend our method to fifth-harmonic generation in a short Ar cell, starting from 12 fs 810 nm pulses, obtaining durations of 11 fs at 162 nm. The energy was sufficient to study the excited-state dynamics of molecules such as ethylene, oxygen, and water, with ≈ 25 times better time resolution than previously.

The setup (Fig. 1) is the same as before [2], supplemented by a monochromator. Briefly, we use a commercial Ti:sapphire laser system, emitting pulses at 810 nm with energy up to 2 mJ, duration of 45 fs, and spectral half-width of 30 nm at a repetition rate of 1 kHz. As described in [8], these pulses are then

broadened to 80 nm (37 THz) by focusing ($f=2$ m) into 500 mbar of Ar and compressed to 12 fs (corresponding to the transform limit) by subsequent reflection from chirped mirrors (Fig. 1a). Part of the resulting radiation, taken aside by a beam splitter, is used as a probe in a pump-probe setup for cross correlation with the VUV beam in a time-of-flight mass spectrometer, in which Xe is ionized by one pump plus three probe photons; additional chirped mirrors are used to compensate the stretching of the 810 nm pulses that arise from the propagation and dispersion in air. This is also done with the other part of the beam.

This other part (12 fs, 710 μ J) is used to generate the VUV pulses (Fig. 1b). It is focused ($f=1$ m) through a short Ar cell (length 18 mm, steel, with two 0.7 mm holes) placed in the focus, where the fifth-

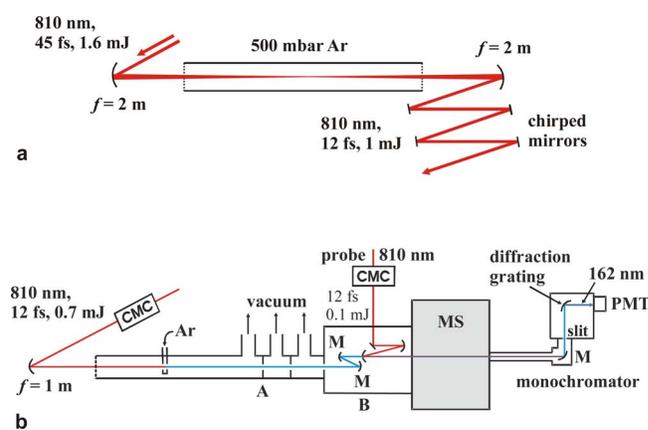


Fig. 1. (Color online) a, Setup for the generation of the 12 fs pulses at 810 nm. The Ar cell is equipped with two 0.25 mm quartz glass windows. b, Setup for the fifth-harmonic generation. The entrance window (CaF_2) is 0.5 mm thick. The probe pulses used for cross correlation in the time-of-flight mass spectrometer (MS) merge with the UV beam at a mirror with a hole. CMC, chirped-mirror compressor; PMT, photomultiplier tube. A is the first of four apertures for differential pumping. B is an evacuated box with mirrors for collimation, focusing, and merging the beams. M, Al mirror for guiding the fifth harmonic in the spectrometer (replaced by dielectric mirrors for the time-resolved measurements).

harmonic radiation is produced. The calculated intensity is $1.9 \times 10^{14} \text{ W cm}^{-2}$ and twice the Rayleigh length of 78 mm. After the cell, the beam propagates under vacuum through several apertures supporting differential pumping of the chambers (details in [2]), through the ionization region of the mass spectrometer and through a CaF_2 window (2 mm) to a scanning monochromator (Acton Research, Model VM-502), which records the spectra. No transmissive optics is used between the Ar cell and the mass spectrometer; three Al mirrors are used to guide the fifth harmonic to the spectrometer. The pressure drops from a few millibars after the Ar cell to $\sim 5 \times 10^{-6}$ mbar in the ionization region and is $< 5 \times 10^{-4}$ mbar in the monochromator. Spectra of both the fifth and the third harmonic are recorded, and the energy of the third harmonic pulses was determined by replacing the monochromator by a power meter.

Figure 2 shows the spectra of the third and fifth harmonic. Their shapes do not change with the Ar pressure p_{Ar} in the short cell. The energies as a function of p_{Ar} are shown in Fig. 3. For the third harmonic, they are measured directly, replacing the monochromator by a power meter (in air). These data then served for calibrating the monochromator readings at the fifth harmonic. The energies initially grow with p_{Ar}^2 , as expected in the perturbative limit. At 270 nm, the maximum (140 nJ, 2×10^{-4} of the input) is at ~ 160 mbar and at the fifth harmonic (≈ 4 nJ, 6×10^{-6}) it is at ~ 50 mbar. Within a factor of 2, the ratio of the two pressures ($160/50 \text{ mbar} = 3.2$) reflects the refractive index difference at the two wavelengths compared to the fundamental, $5(n_{162} - n_{810})/3(n_{270} - n_{810}) = 6$. ($5/3$ is the ratio of the two harmonic frequencies. Any plasma contribution to the refractive index is not taken into account.) This means that the efficiency decrease at higher p_{Ar} is caused by the loss of phase matching. At even higher pressure or on further propagation in Ar, the relative phases of the fundamental and the third harmonic are locked at 90° , as shown in [9,10], so that the efficiency does not recover at higher p_{Ar} . This is also the

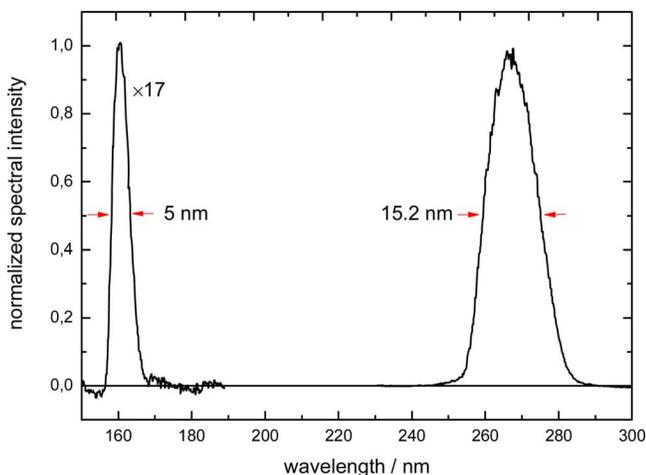


Fig. 2. (Color online) Fifth- and third-harmonic spectra recorded with 20 mbar of Ar in the short cell.

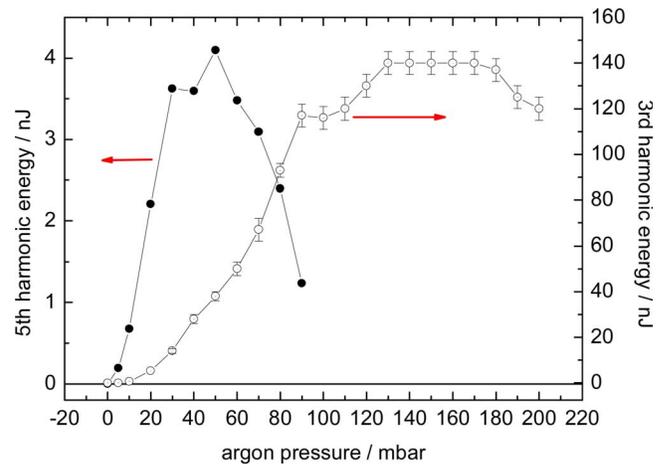


Fig. 3. (Color online) Pulse energies at the fifth (solid circles) and third (open circles) harmonic versus the Ar pressure p_{Ar} in the cell. The gas flow is small enough that p_{Ar} reflects the real pressure.

case at the fifth harmonic (not quantitatively measured). It is also remarkable that at 50 mbar the yield of the VUV radiation is by only a factor of 10 smaller than that of the third harmonic, while this factor even decreases to 2 at < 20 mbar. Finally, the ratio of the spectral half-widths of the fundamental and the fifth harmonic $\Delta\nu_{162}/\Delta\nu_{810} = 57/37 \text{ THz} = 1.54$, which is 30% smaller than $\sqrt{5}$, the value expected in the perturbative limit. (The bandwidth, 63 THz, of the third harmonic in Fig. 2 is, by almost a factor of $\sqrt{3}$, larger than that of the fundamental.)

The maximum energy of the fifth harmonic (≈ 4 nJ at 162 nm) is derived from the comparison of the two spectra of Fig. 2, taking into account the efficiency of the diffraction grating and the photomultiplier and the estimated reflectivity of the three Al mirrors ($\approx 50\%$ each at 162 nm) in Fig. 1b. (Dielectric mirrors were used for the time-resolved experiments). This value is only a lower bound of the feasible energy: the 270 nm energy measured directly after the Ar cell is up to $1 \mu\text{J}$ (as also in [2]), 7 times higher than what arrives at the monochromator. Obviously the losses are caused by the apertures, which served for maintaining the differential pumping. Although their diameters were large enough to transmit all divergent beams (fundamental and harmonics), the possibility for their alignment was limited in the stiff vacuum setup. Optimizing the design for maximum optical transmission could thus improve the energy by up to a factor of 7. Another large factor can perhaps be gained by replacing Ar by Ne: its much smaller dispersion would permit a higher pressure without loss of phase matching, and its much smaller ionization probability allows tighter focusing and higher intensities, which would probably overcompensate its smaller nonlinearity. However, both possibilities require checking by experiment.

The spectral half-width of the fifth-harmonic pulses is ~ 5 nm (57 THz), as already mentioned. This would sustain a pulse duration of ~ 7.7 fs. To determine the duration of the VUV pulses, we apply a cross-correlation scheme, where Xe (ionization en-

ergy 12.15 eV) is ionized by absorption of one VUV (7.65 eV) and three IR (1.53 eV) photons. The two curved dielectric mirrors that replace M in chamber B (Fig. 1b) suppress the third harmonic (3ω) and fundamental (ω) by a factor of >100 , so that ionization by $3\omega+5\times\omega$ or $2\times3\omega+2\times\omega$ is negligible. Also the pump-probe experiments with molecules, resonant at 5ω , confirm that the pulse duration is that of 5ω . Furthermore, the time-resolved (Xe^+) signals show the p_{Ar} dependence as that of the fifth harmonic in Fig. 3. Figure 4 shows this Xe ion signal as a function of the delay time between the VUV and the fundamental pulses as well as the cross-correlation fitting curve resulting from the first power of the VUV and the third power of the probe pulses. The temporal half-width of the Xe^+ signal is ≈ 13 fs, so that the fifth-harmonic pulse duration is 11 ± 1 fs. This corresponds to ~ 1.4 times the transform limit, whereas the 12 fs fundamental pulses are transform limited. A chirp of the VUV pulses might be caused by cross-phase modulation with the fundamental, and an additional lengthening by the residual group delay dispersion of the dielectric mirrors; these mirrors have not been optimized for minimum dispersion (as was also the case for the third harmonic in [2]). A further source of a chirp can be intrinsic in harmonic generation [7]. Sekikawa *et al.* [7], using a setup with the focus after a Xe cell, obtained a negative chirp at 160 nm and used it for pulse compression by a normally dispersive material (LiF).

To conclude, direct fifth-harmonic generation from 12 fs 810 nm pulses in a short Ar cell produces ultrashort VUV pulses at 162 nm with duration of 11 fs as determined by cross correlation with the fundamental in a pump-probe setup with ionization detection. Even shorter pulses are expected, if shorter fundamental pulses are employed. The path in the Ar was short enough to avoid phase mismatch; hence, this setup should also allow sum-frequency generation (for example, adding tunable radiation to short fundamental pulses), which would be simpler than the previous [6,11–16] four-wave difference-

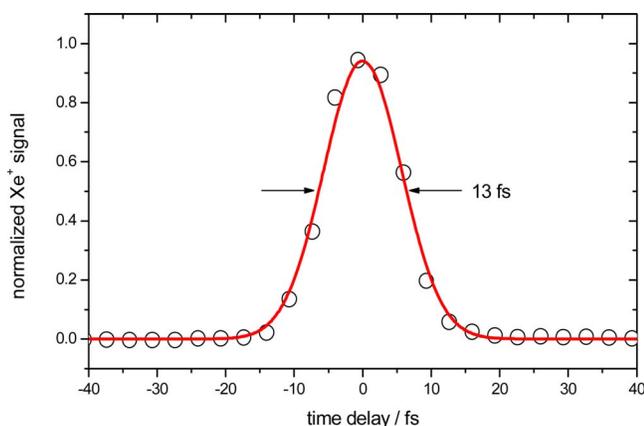


Fig. 4. (Color online) Cross correlation of the fifth-harmonic and IR pulses, resulting from ionization of Xe by 1 VUV+3 IR photons. The smooth curve is a fit using Gaussians for the VUV and IR pulses.

frequency mixing. (However, we do not exclude that four-wave mixing might also contribute in our experiment.) The pulse energy (≈ 4 nJ) was sufficient for pump-probe experiments, even if there was no one-photon resonance (e.g., with Xe and Ar for cross correlation), and there is room for further optimization. The much improved time resolution (13–14 fs as compared to the previous [4,5] 330–450 fs) allowed us to detect coherent oscillations and short time constants in the excited-state dynamics of ethylene [17] and time constants as short as 1.8 and 3.8 fs in photodissociation of water and oxygen [18].

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