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53-attosecond X-ray pulses reach the carbon K-edge

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The motion of electrons in the microcosm occurs on a time scale set by the atomic unit of time—24 attoseconds. Attosecond pulses at photon energies corresponding to the fundamental absorption edges of matter, which lie in the soft X-ray regime above 200 eV, permit the probing of electronic excitation, chemical state, and atomic structure. Here we demonstrate a soft X-ray pulse duration of 53 as and single pulse streaking reaching the carbon K-absorption edge (284 eV) by utilizing intense two-cycle driving pulses near 1.8-μm center wavelength. Such pulses permit studies of electron dynamics in live biological samples and next-generation electronic materials such as diamond.

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High-energy photon bursts, emitted from a gas ensemble at every half optical cycle within an intense laser electric field, form an attosecond pulse train[1]. Upon restricting these bursts to within one-half cycle of the laser field, a single attosecond pulse may be isolated, demonstrating great importance to the study of electron dynamics in pump-probe experiments[2]. Prior to this study, isolated attosecond pulses (IAPs) were primarily generated using few-cycle near-infrared (NIR) Ti:Sapphire lasers with sub-cycle gating technique, such as amplitude gating[3], polarization gating[4], double optical gating[5], and the attosecond lighthouse[6]. The center photon energy and bandwidth of the generated IAPs are limited to within 100 eV and a few tens of eV, respectively, which has permitted the generation of pulse duration as short as 130 as in 2006[7], later 80 as in ref. [3], and then 67 as in ref. [8], as characterized using photoelectron streaking and phase retrieval techniques[9–11]. These first-generation attosecond light sources offered unprecedented temporal resolution in observing and controlling electron and nuclear dynamics in atoms, molecules, and condensed matter. Recently, attosecond band-gap dynamics were observed in silicon in transient absorption experiments near the Si L-edge at ~100 eV[12]. Applying this method to next-generation semiconductor materials such as diamond and graphene requires photon energies surpassing the carbon K-edge (284 eV). Further scaling up of center photon energies and bandwidth, as well as shortening attosecond pulse duration, are technically difficult using 800 nm driving lasers.

The foundation of attosecond light sources is high-order harmonic generation (HHG). It was demonstrated in 2001 that the cutoff of the high harmonic spectrum can be extended dramatically by increasing the driving laser wavelength[13]. The longer period of long-wavelength driving lasers allows an ionized electron more time to be accelerated to a higher kinetic energy in the continuum before recombination with its parent ion, thus leading to higher cutoff photon energies (proportional to the square of the wavelength) when compared to shorter-wavelength NIR drivers. Significant efforts have been made to understand the scaling of the conversion efficiency with longer driving laser wavelengths[14]. Phase matching has also been investigated to overcome the decrease in HHG conversion efficiency due to quantum diffusion effects and the reduction in the recombination cross section[15]. Recent development of carrier-envelope phase (CEP)-stabilized few-cycle lasers at 1.6–2.1 μm paved the way for the next generation of attosecond light sources. CEP-controlled, soft X-ray pulses reaching the water window (284–530 eV) have been generated using these driving lasers[16, 17], and evidence of IAPs therefrom were demonstrated[18–20]. However, no streaking measurement for characterizing the temporal profile of the attosecond pulse in the water window has been reported.

Here we report attosecond streaking measurements of soft X-ray IAPs crossing the boundary of the water window. Implementing the polarization gating technique, we demonstrate the temporal characterization of the soft X-ray pulses with a record of 53 as.

Results

Attosecond Streak Camera. The experimental set-up is shown in Fig. 1. HHG is driven by a home-built 1 kHz, CEP-stabilized, optical parametric chirped pulse amplifier system with an output of 12 fs (two-cycle) pulses near 1.8 μm[21]. The infrared (IR) beam is split into two arms. The first, high-energy arm (90% of the 1.5 mJ energy) passes through polarization gating optics[20]. The laser beam, now with a time-dependent ellipticity is loosely focused ($f = 450$ mm) into a 1.5 mm-long neon gas cell to generate isolated soft X-ray pulses[20]. Tin filters are inserted to block the residual IR beam and to compensate the chirp of the attosecond pulses[22]. Using a grazing-incidence, nickel-coated toroidal mirror, the soft X-ray beam is focused through a hole-drilled mirror, which also re-introduces the second, low-energy IR arm (10% of the 1.5 mJ energy) with a variable time delay. The combined soft X-ray and IR pulses are focused onto a helium or neon detection gas jet to generate photoelectrons, which are collected by a 3-meter-long magnetic-bottle electron time-of-flight (TOF) spectrometer[23]. The interference fringes from a 532 nm CW laser co-propagated through both arms are used to feedback control a piezo-electric transducer that controls and stabilizes the time delay between the soft X-ray and the streaking pulses.

Polarization gating for isolating the attosecond pulses. Polarization gating has been proven a robust scheme for generating broadband IAPs using two-cycle Ti:Sapphire lasers[24]. It takes advantage of the ellipticity dependence of the HHG yield, which becomes even more effective as the driving laser wavelength increases[20]. The polarization optics in Fig. 1 convert a linearly polarized laser pulse into one within which the field polarization changes from circular to linear and back to circular. Streaking traces are taken for different polarization gate widths (Supplementary Fig. 1) to determine the optimal parameters of the polarization optics. IAPs are observed when the width of the linearly polarized gate is less than half of a laser cycle.

One of the challenges of conducting attosecond streaking near the carbon K-edge is the extremely low photon flux of the soft X-ray emission and the small absorption cross section of the detection gas within the soft X-ray photon energy range. The soft X-ray photon flux should be optimized to produce sufficient photoelectrons to construct streaking traces with a reasonable signal-to-noise ratio. Figure 2 shows the polarization-gated soft X-ray spectra at different gas cell pressures measured by the electron TOF. A generation pressure of 1 bar is chosen as a compromise between signal strength, spectral width, and load on

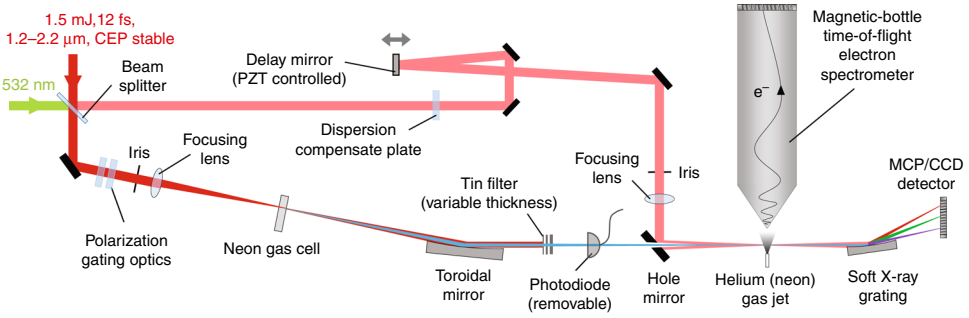

Fig. 1 Experimental set-up. Schematic illustration for isolated attosecond X-ray pulse generation and characterization. CCD charge-coupled device; MCP microchannel plate, PZT piezo-electric transducer

the turbo pumps. The decrease of cutoff photon energy at high gas pressure is likely caused by ionization-induced plasma defocusing, which decreases the laser intensity at the interaction region and shortens the extension of the plateau harmonics[25].

53-attosecond pulses retrieved by PROOF method. The streaked photoelectron spectrum as a function of delay between the soft X-ray pulse and the streaking IR pulse is measured and depicted in Fig. 3a. Helium is used as the detection gas to avoid the contribution of multiple valence orbitals to the photoelectron spectrum. Despite its low absorption cross section for the soft X-ray pulse, the momentum shift of photoelectron is clearly visible across the whole photoelectron spectrum from 100 to 300 eV, indicating the generation of an IAP into the water window.

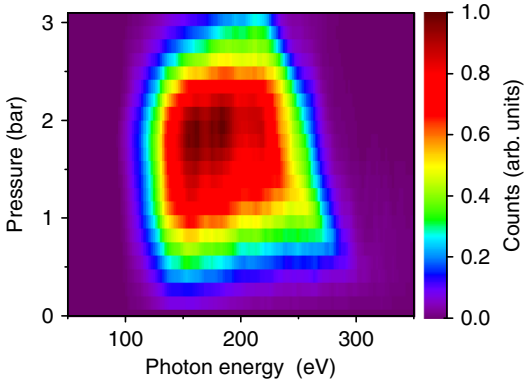

Fig. 2 Pressure-dependent soft X-ray yield. Soft X-ray continua generated by polarization gating as a function of pressure in the neon gas cell. The spectra were recorded by an electron TOF spectrometer and corrected for the photoionization potential (21.6 eV) and absorption cross section of the neon detection gas. Photons with energy <100 eV were filtered out using a 100 nm tin filter

To characterize such a broadband IAP, the phase retrieval by omega oscillation filtering (PROOF) technique is implemented[11]. In PROOF, the photoelectron spectrogram is broken down into its primary Fourier components:

$$I(\nu,\tau) \approx I_o(\nu) + I_\omega(\nu,\tau) + I_{2\omega}(\nu,\tau) \quad (1)$$

where I_o does not change with delay τ, I_ω, and $I_{2\omega}$ oscillate with the streaking laser frequency ω and twice the frequency 2ω, respectively, and ν is the photoelectron momentum. While the soft X-ray spectrum is directly measured by the TOF spectrometer, the unknown spectral phase is encoded in $I_\omega(\nu,\tau)$. During the retrieval, the amplitude and phase of the soft X-ray pulses, depicted in Fig. 3c, d, are guessed iteratively in PROOF to match

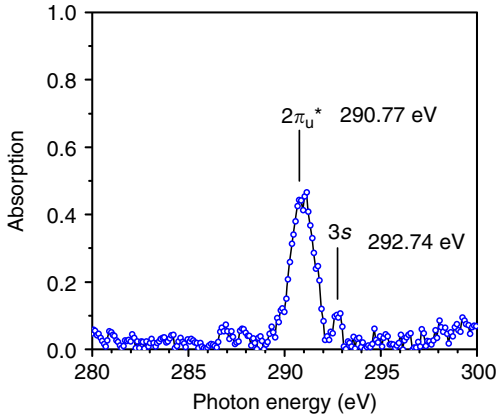

Fig. 4 Carbon dioxide K-shell photoabsorption spectrum. The two absorption peaks correspond to $C_{1s} \rightarrow 2\pi_u^*$ and $C_{1s} \rightarrow$ Rydberg 3s state[26]. Carbon dioxide gas with 25 torr·mm pressure-length product is used in this measurement

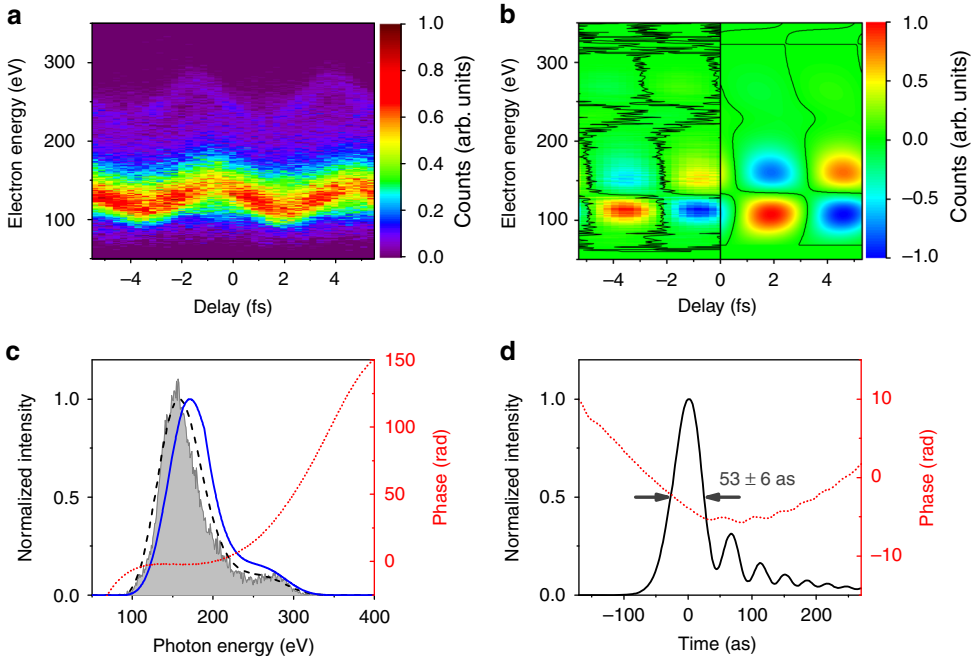

Fig. 3 PROOF retrieved 53 as soft X-ray pulse. **a** Photoelectron spectrogram as a function of temporal delay between the soft X-ray and the streaking IR pulses in the case of a 400-nm-thick tin filter. A negative delay corresponds to an earlier IR pulse arrival. **b** Filter I_ω trace (−5 to 0 fs) from the spectrogram in **a** and the retrieved I_ω trace (0–5 fs). **c** Experimentally recorded (*gray shade*) and PROOF-retrieved spectra (*black dash*) by adding helium photoionization potential (24.6 eV); corrected photon spectrum (*blue solid*), and spectrum phase (*red dot*) from PROOF. **d** Retrieved temporal intensity profile and phase of the 53 as pulses

the retrieved modulation depth and phase angle of I_ω of the measured trace (Fig. 3b).

The thickness of the tin filter in this measurement is 400 nm. We experimented with different filter thicknesses to demonstrate that a 400-nm-thick tin filter is the best for compensating the atto-chirp under our experimental conditions (Supplementary Fig. 3). However, only the spectral phase error in the low-energy part (<200 eV) of the tin filter transmission window can be well-compensated because the filter's group delay dispersion approaches zero at 300 eV (Supplementary Fig. 2). This is confirmed in Fig. 3a, b, as the up-streaking excursion in the high-energy section above 200 eV is asymmetric horizontally with respect to the turning point of the streaking trace, while the trace below 200 eV is symmetric. The PROOF retrieval also shows a parabolic phase above 200 eV (red dot in Fig. 3c). The retrieved pulse duration full width at half maximum (FWHM) reaches 53 as (transform limited 20 as), which is less than the shortest attosecond pulses achieved with Ti:Sapphire driving lasers. Further increase of the filter thickness leads to an over-compensated chirp for low-energy photons, resulting in a longer pulse duration (Supplementary Fig. 3). The soft X-ray photon flux was measured with an extreme ultraviolet (XUV) photodiode for HHG using the linearly polarized driving field. Knowing the relative intensity change between the ungated and gated HHG, as well as the tin filter transmission, the photon flux for the 53 as pulse is estimated to be $\sim 5 \times 10^6$ photons per laser shot. The photon flux above carbon K-edge (284 eV) is $> 1 \times 10^5$ photons per laser shot.

K-edge X-ray absorption of carbon dioxide molecule. To demonstrate the applicability of our water window attosecond source, a carbon K-edge absorption experiment was performed. The gas jet in Fig. 1 was replaced with a 1 mm-long gas cell filled with 25 torr carbon dioxide. A 2400 lines/mm soft X-ray grating and an X-ray CCD camera were chose to achieve high spectrum resolution near carbon K-edge. We integrated for 4 minutes to extract the absorption spectrum shown in Fig. 4. The main absorption peak at 290.77 eV corresponds to the transition from carbon ground state 1*s* to the lowest unoccupied molecular orbital $2\pi_u^*$, while the satellite peak at 292.74 eV corresponds to the excitation to the Rydberg 3*s* orbital[26]. Access to these absorption features allows for the tracing of the temporal evolution of valence π- or σ-bonding electrons in bio-molecules. Such broadband and ultrashort attosecond pulses combined with X-ray absorption near-edge spectroscopy techniques will become powerful tools for studying ultrafast charge dynamics in molecules and condensed-matter targets containing carbon.

Aiming to control chemical reactions via manipulating electron dynamics in molecules with ultrashort laser pulses[27], attosecond water window X-rays will also play an important role in the emerging field of attochemistry. Charge migration, a process strongly affecting chemical reactivity, occurs on sub to few femtosecond time scale[28, 29]. Water window attosecond pulses are unique tools for measuring the charge distribution in molecules containing carbon/oxygen atoms and exploring the possibility to predetermine chemical reaction path by controlling the initial charge migration step[27].

Discussion

In summary, we have shown the generation and characterization of isolated soft X-ray pulses. With the shortest pulse duration decreased by 20%, the spectral range (100–330 eV) where the high harmonic pulses have been characterized in the time domain is doubled. We also determined experimentally and quantitatively that the attosecond pulse duration is limited by the chirp instead of the bandwidth in the new spectral region. The bandwidth tunability (10–150 eV) of previously demonstrated IAPs has already proven worthwhile in their applications to the study of inner-shell or valence-electron dynamics. The extremely broad bandwidth (100–330 eV) of the 53 as pulses covers the boron K-edge (188 eV) as well as the carbon K-edge. Very recently, time-resolved X-ray transient absorption in the water window has been demonstrated to observe light-induced chemical reactions in CF_4 and other molecules with temporal resolution limited to 40 fs[30]. The X-ray source demonstrated in this work makes it practical to observe charge migration by exploiting transition from the carbon core level to the unoccupied valence orbitals at the carbon K-edge (Fig. 4), similar to that demonstrated in ref. [30] but with attosecond resolution. Such attosecond sources—synchronized with few-cycle IR fields or high-energy XUV pulses—will bring opportunities to study biological or chemical science and strong-field physics.

Data availability. The authors declare that the main data supporting the findings of this study are available within the article and its Supplementary Information files. Extra data are available from the corresponding author upon request.

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References

1. Paul, P. M. et al. Observation of a train of attosecond pulses from high harmonic generation. *Science* **292**, 1689–1692 (2001).
2. Hentschel, M. et al. Attosecond metrology. *Nature* **414**, 509–513 (2001).
3. Goulielmakis, E. et al. Single-cycle nonlinear optics. *Science* **320**, 1614–1617 (2008).
4. Corkum, P., Burnett, N. & Ivanov, M. Y. Subfemtosecond pulses. *Opt. Lett.* **19**, 1870–1872 (1994).
5. Mashiko, H. et al. Double optical gating of high-order harmonic generation with carrier-envelope phase stabilized lasers. *Phys. Rev. Lett.* **100**, 103906 (2008).
6. Kim, K. T. et al. Photonic streaking of attosecond pulse trains. *Nat. Photonics* **7**, 651–656 (2013).
7. Sansone, G. et al. Isolated single-cycle attosecond pulses. *Science* **314**, 443–446 (2006).
8. Zhao, K. et al. Tailoring a 67 attosecond pulse through advantageous phase-mismatch. *Opt. lett.* **37**, 3891–3893 (2012).
9. Itatani, J. et al. Attosecond streak camera. *Phys. Rev. Lett.* **88**, 173903–173903 (2002).
10. Mairesse, Y. & Quéré, F. Frequency-resolved optical gating for complete reconstruction of attosecond bursts. *Phys. Rev. A* **71**, 011401 (2005).
11. Chini, M., Gilbertson, S., Khan, S. D. & Chang, Z. Characterizing ultrabroadband attosecond lasers. *Opt. Express* **18**, 13006–13016 (2010).
12. Schultze, M. et al. Attosecond band-gap dynamics in silicon. *Science* **346**, 1348–1352 (2014).
13. Shan, B. & Chang, Z. Dramatic extension of the high-order harmonic cutoff by using a long-wavelength driving field. *Phys. Rev. A* **65**, 011804 (2001).
14. Tate, J. et al. Scaling of wave-packet dynamics in an intense midinfrared field. *Phys. Rev. Lett.* **98**, 013901 (2007).
15. Takahashi, E. J., Kanai, T., Ishikawa, K. L., Nabekawa, Y. & Midorikawa, K. Coherent water window X ray by phase-matched high-order harmonic generation in neutral media. *Phy. Rev. Lett* **101**, 253901 (2008).
16. Ishii, N. et al. Carrier-envelope phase-dependent high harmonic generation in the water window using few-cycle infrared pulses. *Nat. Commun* **5**, 3331 (2014).
17. Keathley, P. D. et al. Water-window soft x-ray high-harmonic generation up to the nitrogen K-edge driven by a kHz, 2.1 μm OPCPA source. *J. Phys. B: At. Mol. Opt. Phys.* **49**, 155601 (2016).
18. Teichmann, S. M., Silva, F., Cousin, S. L., Hemmer, M. & Biegert, J. 0.5-keV Soft X-ray attosecond continua. *Nat. Commun.* **7**, 11493 (2015).
19. Silva, F., Teichmann, S. M., Cousin, S. L., Hemmer, M. & Biegert, J. Spatiotemporal isolation of attosecond soft X-ray pulses in the water window. *Nat. Commun.* **6**, 6611 (2015).
20. Li, J. et al. Polarization gating of high harmonic generation in the water window. *Appl. Phys. Lett.* **108**, 231102 (2016).

21. Yin, Y. et al. High-efficiency optical parametric chirped-pulse amplifier in BiB_3O_6 for generation of 3 mJ, two-cycle, carrier-envelope-phase-stable pulses at 1.7 μm. *Opt. Lett.* **41**, 1142–1145 (2016).
22. Mairesse, Y. et al. Attosecond synchronization of high-harmonic soft x-rays. *Science* **302**, 1540–1543 (2003).
23. Zhang, Q., Zhao, K. & Chang, Z. High resolution electron spectrometers for characterizing the contrast of isolated 25 as pulses. *J. Electron Spectrosc. Relat. Phenom* **195**, 48 (2014).
24. Sola, I. J. et al. Controlling attosecond electron dynamics by phase-stabilized polarization gating. *Nat. Phys.* **2**, 319–322 (2006).
25. Altucci, C. et al. Influence of atomic density in high-order harmonic generation. *J. Opt. Soc. Am. B* **13**, 148–156 (1996).
26. Tronc, M., King, G. C. & Read, F. H. Carbon K-shell excitation in small molecules by high-resolution electron impact. *J. Phys. B: At. Mol. Phys.* **12**, 137 (1979).
27. Golubev, N. V., Despré, V. & Kuleff, A. I. Quantum control with smoothly varying pulses: general theory and application to charge migration. *J. Mod. Opt.* **64**, 1031–1041 (2017).
28. Remacle, F. & Levine, R. D. An electronic time scale in chemistry. *Proc. Natl Acad. Sci. USA* **103**, 6793–6798 (2006).
29. Attar, A. R. et al. Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction. *Science* **356**, 54–59 (2017).
30. Pertot, Y. et al. Time-resolved x-ray absorption spectroscopy with a water window high-harmonic source. *Science* **355**, 264–267 (2017).

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Author contributions

Z.C. conceived and supervised the study. X.R., Y.Y., J.L., E.C., and Y.W. developed the laser source. J.L. and X.R., (in cooperation with A.C., Y.C., Y.W., and S.H.) prepared and performed the experiment. M.C., K.Z., and J.L. performed simulations and pulse retrieval. J.L. and Z.C. wrote major parts of the manuscript. All authors discussed the results and contributed to the final manuscript.

Additional information

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Erratum: 53-attosecond X-ray pulses reach the carbon K-edge

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This Article contains an error in the final two sentences of the section entitled "53-attosecond pulses retrieved by PROOF method". These sentences should read: 'Knowing the relative intensity change between the ungated and gated HHG, as well as the tin filter transmission, the photon flux for the 53 as pulse is estimated to be ~ 5×10^5 photons per laser shot. The photon flux above carbon K-edge (284 eV) is $>1 \times 10^4$ photons per laser shot'.

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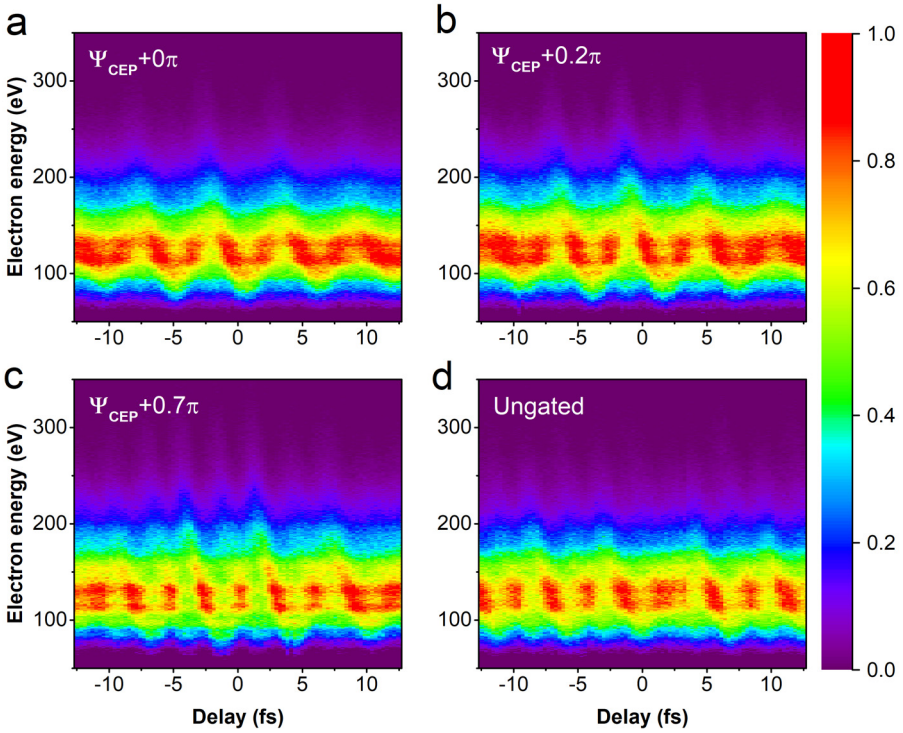
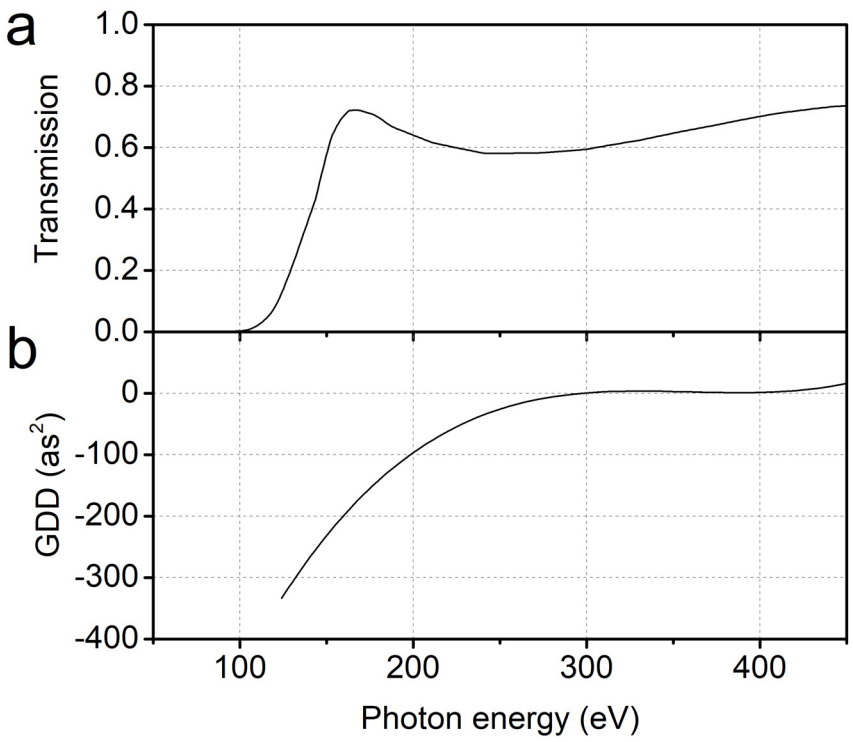
Description of Supplementary Files

File name: Supplementary Information
Description: Supplementary figures, supplementary notes and supplementary references.

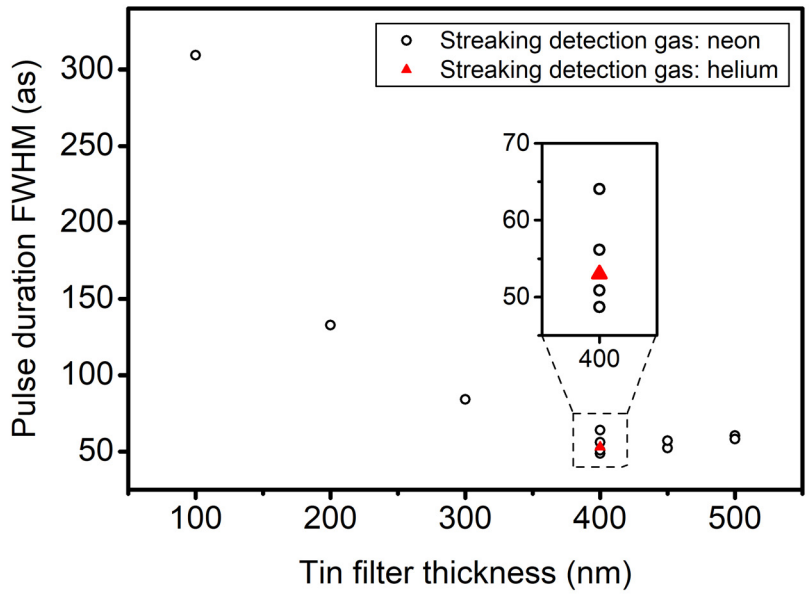
File name: Peer review file



Supplementary Figure 1: Carrier-envelope phase influence on polarization gating. Experimental streaked photoelectron spectrograms using polarization gating (gate width δt_{G1}=3.6 fs) under different carrier-envelope phase (CEP) values (**a** to **c**), with the ungated case (**d**) shown for comparison. The fundamental IR field was filtered out using 100 nm tin filter for all cases.



Supplementary Figure 2: Transmission and group delay dispersion of tin filter. Calculated transmission (a) and group delay dispersion (GDD) (b) of 100 nm tin filter.



Supplementary Figure 3: Atto-chirp compensation by tin filter. PROOF-retrieved attosecond pulse duration with dipole correction at different filter thicknesses.

Supplementary Note 1: Laser system

The experiments are performed with an optical parametric chirped pulse amplifier (OPCPA) system at a 1 kHz repetition rate [1]. The front-end pump laser for the OPCPA is a home-built Ti:Sapphire chirped pulse amplifier (CPA) system with synchronized output of 2.2 mJ, 30 fs pulses and 18 mJ, 5 ps pulses. The 2.2 mJ pulses are focused into a neon-filled hollow-core fiber for white light generation. The white light pulses (0.5–0.9 μm) are compressed to 7 fs using chirped mirror pairs and then focused into a BIBO crystal for intra-pulse difference-frequency mixing [2]. This yields a broadband IR (1.2–2.2 μm) seed pulse with passive CEP stability. These IR seed pulses are stretched to 4.4 ps using an acousto-optic programmable dispersive filter (AOPDF) [3] and amplified inside three BIBO-based OPCPA stages, which are pumped by the synchronized output of the 18 mJ, 5 ps pulses from the Ti:Sapphire CPA system. The amplified IR pulses are compressed to 12 fs using the material dispersion of bulk fused silica. We use the AOPDF to fine-tune the dispersion and CEP of the IR pulses. The available IR pulse energy delivered to the experiments was more than 1.5 mJ.

Supplementary Note 2: Polarization gating for generating isolated attosecond pulses

The polarization gating setup in this experiment consists of two birefringent plates [4]. The optical axis of the first quartz plate is set to 45° with respect to the polarization of the incoming driving pulse. A delay T_d is introduced between the o- and e-pulses due to the refractive index difference between the o- and e-axes of quartz. The value of T_d can be controlled by changing the thickness of the quartz plate. The second zero-order quarter wave plate (optical axis set at 0°) converts the o- and e-pulses into counter-rotating circularly-polarized pulses. The electric field becomes linearly-polarized in the middle of the overlapped region and elliptically-polarized elsewhere. Effective HHG is only allowed in the linear portion of the pulse with a polarization gate width given by [5]:

$$\delta t_G = \varepsilon_{th} \tau_p^2 (\ln(2) T_d)^{-1}$$

where $\varepsilon_{th}=0.1$ is the threshold ellipticity for HHG using our driving field [6] and $\tau_p=12$ fs is the pulse duration of our driving field.

We tested the polarization gate choosing $T_{d1}=T_0$, where $T_0=5.7$ fs is the laser optical period. This leads to a gate width $\delta t_{G1}=3.6$ fs$>T_0/2$. Since the HHG process repeats every half laser cycle for linearly-polarized driving field, a gate width $\delta t_{G1}>T_0/2$ could lead to more than one attosecond burst. We recorded streaked photoelectron spectrogram using polarization gating of $\delta t_{G1}=3.6$ fs at different CEP values and compared with ungated condition (Supplementary Fig. 1).

The streaked photoelectron spectrogram in Supplementary Fig. 1a shows a clear sinusoidal energy shift with a period of T_0. Upon changing the relative CEP value by only 0.2 π, half-cycle streaking becomes obvious in the upward and downward side of the energy shift (Supplementary Fig. 1b). Such a half-cycle energy shift is a signature of double attosecond pulses generated inside the polarization gate [7]. An even stronger half-cycle energy shift is observed when further changing the relative CEP value (Supplementary Fig. 1c). Such half-cycle energy shift would lead to a significant Fourier component $I_{2\omega}(v,\tau)$ to the photoelectron spectrogram. In order to suppress the double pulses, we applied polarization gating using a shorter gate width δt_{G2}=1.8 fs<T_0/2 with optimized CEP values. The resulted 2ω component $I_{2\omega}(v,\tau)$ is more than 10 times smaller than the ω component $I_{\omega}(v,\tau)$, which confirms the presence of an isolated attosecond pulse for all streaking experiments reported in this paper.

Supplementary Note 3: Atto-chirp compensation and error bar for streaking measurement

It is known that the attosecond pulses generated by HHG are not transform-limited in their temporal duration [8]. At the microscopic level, two quantum trajectories of the laser-driven electron contribute to the high-harmonic pulse emission. Typically only the short trajectory is phase-matched in experiments. The chirp is positive for emissions from the short trajectory, which can potentially be compensated by the negative dispersion of a tin filter in the region of 100 to 300 eV [9]. However, the group delay dispersion (GDD) of tin approaches zero at 300 eV (Fig. S2), meaning that atto-chirp compensation is only effective for the lower energy part (< 200 eV) of the spectrum.

Supplementary Fig. 3 shows the retrieved attosecond pulse durations versus the tin filter thickness. Neon gas was first used as the detection gas for its relatively-large absorption cross-section compared to helium. We combined several tin filters to find the optimum thickness for atto-chirp compensation. A clear trend of decreasing pulse durations is found as the filter thickness increases from 100 to 400 nm. Further increasing filter thickness to 500 nm led to an overcompensated atto-chirp on the low energy side, resulting in a slightly increased pulse duration. Multiple measurements are repeated at 400 nm, 450 nm and 500 nm thickness to confirm the experimental repeatability. At a thickness of 400 nm, a total of 5 measurements are performed and presented. A standard deviation of 6 as (calculated from the 5 results at 400 nm) is used for the error bar in Fig. 3 in the main text, which represents the repeatability of our measurement.

Supplementary Note 4: Retrieval procedure in PROOF

In PROOF, the spectrum and phase of the attosecond photoelectron burst are retrieved using an iterative algorithm, the goal of which is to minimize the error between the component of the experimental spectrogram oscillating with the laser frequency ($I_{\omega}(v,\tau)$ in Eq. (1) of the main text), and a guessed trace, given by Eq. (11) in Ref. 11. $I_{\omega}(v,\tau)$ can be written as the product of two components: a modulation amplitude $\gamma(v)$ and the laser-frequency oscillation component

sin[ωτ+α(v)], where *α(v)* describes the phase of the oscillation. Both *γ(v)* and *α(v)* epend on (and can be calculated from) the spectral amplitude and phase of the attosecond burst.

In the algorithm, the error between the experimental and guessed *γ(v)* and *α(v)* are separately minimized, in an iterative fashion. The algorithm proceeds as follows:

Initialization: Let the spectral amplitude of the attosecond photoelectron burst be given by $U(v)=(I_o(v))^{1/2}$, where $I_o(v)$ is the DC Fourier component of the experimental spectrogram. This is a very accurate guess in the case where the streaking intensity is low; however, it must be refined by further iteration (spectrum optimization) under practical experimental conditions. To avoid introducing noise into the algorithm, the spectrum is smoothed using a cubic spline fitting function.

Phase optimization: Guess the spectral phase of the attosecond burst $\phi(v)$ which minimizes the error function between the experimentally-obtained phase angle *α(v)* and that calculated from the guessed *U(v)* and $\phi(v)$. For this minimization, the value of the phase at each electron energy is allowed to vary between 0 and 2π, and the spectral phase function $\phi(v)$ is obtained by unwrapping the phase and applying a cubic spline fitting before evaluating the error function, in order to avoid introducing noise into the algorithm.

Spectrum optimization: Guess the spectral amplitude of the attosecond burst *U(v)* which minimizes the error function between the experimentally-obtained modulation amplitude *γ(v)* and that calculated using the guessed *U(v)* and *γ(v)*. For this minimization, the value of the amplitude is allowed to vary freely, and the spectral amplitude function *U(v)* is obtained by applying a cubic spline fitting before evaluating the error function, in order to avoid introducing noise into the algorithm.

Repeat phase and spectrum optimization iteratively. After each iteration, evaluate the error function between the experimentally obtained laser-frequency filtered spectrogram $I_\omega(\nu,\tau)$ and that calculated using the guessed *U(v)* and $\phi(v)$. Once the error has decreased to a suitable value, stop the loop and export the guessed *U(v)* and $\phi(v)$. Apply the dipole correction to the guessed *U(v)* and $\phi(v)$ to obtain the attosecond photon pulse spectrum and phase.

The metrics used to evaluate the accuracy of the retrieval are therefore the agreement between the filtered spectrogram $I_\omega(v,\tau)$ and that calculated from the guessed *U(v)* and $\phi(v)$, as well as the agreement between the measured and guessed photoelectron spectrum. The agreement in Fig. 3(b) is excellent, with the only discrepancy occurring in the photoelectron spectral region around 225 eV, where the experimental modulation amplitude drops to nearly zero, and the phase angle cannot be accurately extracted.

Supplementary References

1. Y. Yin, J. Li, X. Ren, K. Zhao, Y. Wu, E. Cunningham, Z. Chang, High-efficiency optical parametric chirped-pulse amplifier in BiB_3O_6 for generation of 3 mJ, two-cycle, carrier-envelope-phase-stable pulses at 1.7 μm. *Opt. Lett.* **41**, 1142-1145 (2016).

2. T. Fuji, A. Apolonski, F. Krausz, Self-stabilization of carrier-envelope offset phase by use of difference-frequency generation. *Opt. Lett*. **29**, 632 (2004).

3. P. Tournois, Acousto-optic programmable dispersive filter for adaptive compensation of group delay time dispersion in laser systems. *Optics Commun*. **140**, 245 (1997).

4. I. J. Sola, E. Mével, L. Elouga, E. Constant, V. Strelkov, L. Poletto, P. Villoresi, E. Benedetti, J.-P. Caumes, S. Stagira, C. Vozzi, G. Sansone, M. Nisoli, Controlling attosecond electron dynamics by phase-stabilized polarization gating. *Nat. Phys*. **2**, 319-322 (2006).

5. V. Strelkov, A Zaïr, O. Tcherbakoff, R. López-Martens, E. Cormier, E. Mével, E. Constant. Single attosecond pulse production with an ellipticity-modulated driving IR pulse. *J. Phys. B* **38**, L161 (2005).

6. J. Li, X. Ren, Y. Yin, Y. Cheng, E. Cunningham, Y. Wu, Z. Chang, Polarization gating of high harmonic generation in the water window. *Appl. Phys. Lett.* **108**, 231102 (2016).

7. J. Gagnon, V. S. Yakovlev, The robustness of attosecond streaking measurements. *Opt. Express* **17**, 17678 (2009).

8. Y. Mairesse, A. De Bohan, L. Frasinski, H. Merdji, L. Dinu, P. Monchicourt, P. Breger, M. Kovačev, R. Taïeb, B. Carré, Attosecond synchronization of high-harmonic soft x-rays. *Science* **302**, 1540-1543 (2003).

9. D. H. Ko, K. T. Kim, C. H. Nam, Attosecond-chirp compensation with material dispersion to produce near transform-limited attosecond pulses. *J. Phys. B* **45**, 074015 (2012).

Reviewers' comments:

Reviewer #1 (Remarks to the Author):

This is a technically impressive paper that demonstrates production of isolated attosecond pulses at high photon energies. The pulses are very short (53 as), and while other groups have claimed to generate attosecond pulses in a similar spectra regime, this paper clearly demonstrates via attosecond streaking that the pulses are indeed isolated attosecond pulses. So as a technical accomplishment the paper is significant. There are, however, a couple of issues that need to be addressed. First, it became apparent only about halfway through the paper that the spectral range of the IAP is mainly below the water window; there appears to be very little intensity above the carbon K-edge. The authors should be a little more forthcoming about this point earlier in the paper. It would also be helpful to estimate the photon flux above 284 eV.
The other aspect of this paper that is a bit strange is that starting on p. 6, a second set of results from a different laser system is presented. There is no information about this system; it is not clear if the only difference is that no double optical gating is used, or if it's a completely different system than that shown in Fig. 1. This part of the paper reads like an add-on. There is no hint of a second system in the abstract, for example. The material here should be better integrated into the rest of the manuscript by, for example, briefly describing the second system as part of the discussion of Fig. 1.
If these issues are addressed, this paper is probably publishable in Nature Communications. The focus of the paper is a bit narrow, covering laser pulse characterization with no application to a model system, but the work is certainly of very high quality.

Reviewer #2 (Remarks to the Author):

The manuscript by Li et al. reports on the production and characterization of isolated attosecond pulses spanning the carbon K-edge around 284 eV. Such a source of soft x-rays is important because of its ability to probe matter using XAFS techniques. Two different laser systems by two teams are employed: UCF (USA) and ICFO (Spain).

The manuscript largely represents a technical achievement. I do not believe that it is appropriate for Nature Communications. Similar studies have been published in Optics Letters.

What is new?

• The generation of an isolated attosecond pulse in the range 130-270 eV (Fig. 2) or 120-220 eV with a tail to 300 eV (Fig. 3c).
• Compensation of the atto chirp below 200 eV using a tin filter.
• Attosecond streaking measurement of the pulse duration at 53 asec.

What has been done previously?

• Popmintchev Science 336, 6086 (2012) – Generation of a spectrum extending to 1.4 keV, composed of a series of attosecond pulses.
• Opt Lett 37, 3893 (2012) [UCF team] – Generation of an isolated 67 asec pulse, 60-150 eV spectrum, using DOG and measured with PROOF.
• Appl Phys Lett 108, 231102 (2016) [UCF team] – same setup as present manuscript, 35-300 eV spectrum. No measurement of pulse duration.
• Opt Lett 18, 5383 (2014) [ICFO team] – Same setup as present manuscript. Spectrum to 400 eV. NEXAFS measurement. Fig 3 same as present Fig. 4a.
• Nat Commun 6, 6611 (2015) [ICFO team] – Same laser setup as present manuscript. Isolated asec pulses with photonic streaking, 230-300 eV spectrum.

In summary, what is new here is the measurement of the pulse duration of 53 asec. All other parts have been done previously at either UCF or ICFO.

Reviewer #3 (Remarks to the Author):

The manuscript by Jie Li et al., entitled as "53-Attosecond X-ray Pulses Glancing Through the Water Window," describes the generation of isolated attosecond pulses in the soft x-ray region, of which the spectrum is extended beyond the carbon K edge, the entrance of the water window (284 - 530 eV).

At UCF, the authors succeed in measuring attosecond spectrograms, which are analyzed by the PROOF method. The spectrograms obtained with Sn filters of different thickness analyzed by the PROOF confirm the effect of filter dispersion and, using a 400-nm-thick Sn filter, the authors confirm the generation of 53-attosecond pulses in the soft x-ray region, which are the shortest light pulses in the world. The results shown in Figs 1 - 3 together with the supplemental information are excellent and worth publishing in Nature Communications.

However, the experimental result (Fig. 4) at ICFO and its interpretation are not convincing. The authors claim the generation of "isolated attosecond" pulses from the streaking spectrogram shown in Fig. 4b. However, the authors do not retrieve the spectrogram to obtain the temporal information of the soft x-ray pulses. Without the pulse duration of the soft x-ray bursts specified, it is inappropriate to use the term "attosecond". Additionally, concerning the term "isolated", the experimental results shown in the manuscript is not enough to claim the isolation of a soft x-ray burst. Please provide CEP dependence of streaking spectrograms and/or high harmonic spectra to estimate the intensity contrast between the primary and satellite pulses.

In summary, the authors are suggested to provide a major revision including additional experimental results to support their claims, modification the interpretation of the experimental results at ICFO, or the removal of the streaking results at ICFO from the manuscript before resubmission for publication.

Response to Reviewer's Comments

We would like to thank all reviewers for their comments, which have been addressed in detail in this response. The manuscript has been revised accordingly.

Reviewer #1 (Remarks to the Author):

Comment 1. This is a technically impressive paper that demonstrates production of isolated attosecond pulses at high photon energies. The pulses are very short (53 as), and while other groups have claimed to generate attosecond pulses in a similar spectra regime, this paper clearly demonstrates via attosecond streaking that the pulses are indeed isolated attosecond pulses. So as a technical accomplishment the paper is significant. There are, however, a couple of issues that need to be addressed. First, it became apparent only about halfway through the paper that the spectral range of the IAP is mainly below the water window; there appears to be very little intensity above the carbon K-edge. The authors should be a little more forthcoming about this point earlier in the paper.

Reply 1: Our photon spectrum peak is indeed below the carbon K-edge. To avoid misleading the readers, we changed the sentence related to spectrum range in the abstract:

"Here we demonstrate a soft X-ray pulse duration of 53 as and single pulse streaking ~~in~~ reaching the "water window" (284 to 530 eV) by utilizing intense two-cycle driving pulses near 1.8-micron center wavelength."

In the paragraph three, we also revise the first sentence:

"Here we report attosecond streaking measurements of soft X-ray IAPs ~~in the water window~~ crossing the boundary of the water window."

Comment 2. It would also be helpful to estimate the photon flux above 284 eV.

Reply 2: We estimate the photo flux > 284 eV is 1/40 of the total flux (100-330 eV) base on our spectrum shape, which gives > 1×10^5 photons per laser shot, or > 1×10^8 photons per second above 284 eV. To the best of our knowledge, this flux is still the highest among all reports that claimed to generate high energy pulse within 284-530 eV:

1. [2016 MIT] 1.5×10^6 photons /s/ 1% bandwidth @350 eV, *J. Phys. B: At. Mol. Opt. Phys.* **49** 155601(2016)
2. [2016 ICFO] 7.3×10^7 photons /s @ 280-550 eV, Nature Communications **7**, 11493 (2016)
3. [2014 University of Tokyo] < 1×10^4 photons /s @ 284 -350 eV, Nature Communications **5**, 3331 (2014)
4. [2014 INRS Canada] 2×10^7 photons/s @ 280-500 eV, UP.2014.09.Wed.P3.49
5. [2012 Colorado] ~ 10^7 photons/s @ 284-530 eV, Science 336, 6086 (2012)

It is worth to point out that the phase and duration of the pulses in these five papers were not characterized. We add the estimated photon flux (>284 eV) to our manuscript:

"Knowing the relative intensity change between the ungated and gated HHG, as well as the tin filter transmission, the photon flux for the 53 as pulse is estimated to be ~5×10^6 photons per laser shot. The photon flux above carbon K-edge (284 eV) is > 1×10^5 photons per laser shot."

Comment 3. The other aspect of this paper that is a bit strange is that starting on p. 6, a second set of results from a different laser system is presented. There is no information about this system; it is not clear if the only difference is that no double optical gating is used, or if it's a completely different system than that shown in Fig. 1. This part of the paper reads like an add-on. There is no hint of a second system in the abstract, for example. The material here should be better integrated into the rest of the manuscript by, for example, briefly describing the second system as part of the discussion of Fig. 1.

Reply 3: We agree with the reviewer that this part reads like an add-on. Similar concerns have been address by reviewer #3. Therefore, we decide to remove the ICFO's experiment from manuscript.

Comment 4. If these issues are addressed, this paper is probably publishable in Nature Communications. The focus of the paper is a bit narrow, covering laser pulse characterization with no application to a model system, but the work is certainly of very high quality.

Reply 4:

To broaden the scope of our paper and demonstrate the potential high impact of the unique x-ray source, we added new results on carbon K-edge absorption experiment with carbon dioxide gas sample. By using a 2400 lines/mm grating and an x-ray CCD camera in the x-ray spectrometer, we reached higher spectrum resolution (~0.1 eV per CCD pixel at 284 eV). We were able to identify absorption peaks from K-shell (1s) to unoccupied orbitals ($2\pi_u^*$), the potential temporal resolution is in the order of attosecond. This result is added to the main text (Fig. 4). The results laid the foundation for time-resolving chemical bond breaking of carbon containing molecules as wells as for studying a broad range of coupled electron-nuclear dynamics in molecules and condensed matter.

Reviewer #2 (Remarks to the Author):

The manuscript by Li et al. reports on the production and characterization of isolated attosecond pulses spanning the carbon K-edge around 284 eV. Such a source of soft x-rays is important because of its ability to probe matter using XAFS techniques. Two different laser systems by two teams are employed: UCF (USA) and ICFO (Spain).

The manuscript largely represents a technical achievement. I do not believe that it is appropriate for Nature Communications. Similar studies have been published in Optics Letters.

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• The generation of an isolated attosecond pulse in the range 130-270 eV (Fig. 2) or 120-220 eV with a tail to 300 eV (Fig. 3c).

• Compensation of the atto chirp below 200 eV using a tin filter.
• Attosecond streaking measurement of the pulse duration at 53 asec.

What has been done previously?

• Popmintchev Science 336, 6086 (2012) – Generation of a spectrum extending to 1.4 keV, composed of a series of attosecond pulses.

Reply 1: This laser is at relative low repetition rate (20Hz), limit the photo flux to ~ 10^7 photons/s at 284-530 eV. More important, only spectra were measured, which indicate pulse trains. They should not be directly compared with our isolated pulses. Their pulses are likely femtosecond pulses instead of attosecond pulses since their driving laser is at 3.9 micron and there was no chirp compensation.

• Opt Lett 37, 3893 (2012) [UCF team] – Generation of an isolated 67 asec pulse, 60-150 eV spectrum, using DOG and measured with PROOF.

Reply 2: The 800 nm driving field gives limited high-harmonic bandwidth (60-150 eV). Pushing attosecond photon energy into the water window is not simply a repeat of what is done with 800 nm laser. To bring the water-window source to the applicable level (or high enough flux for experiment), many teams are developing new driving laser sources and testing optimal gating methods. We believe our technique achieved the highest photon flux in the water window (see replay 2 for reviewer #1) with the shortest isolated pulse. Which is a milestone in attosecond research.

• Appl Phys Lett 108, 231102 (2016) [UCF team] – same setup as present manuscript, 35-300 eV spectrum. No measurement of pulse duration.

Reply 3: In our APL paper, the CEP effect indicates isolated attosecond pulses are generated. However, the isolated attosecond pulse should only be demonstrated by streaking experiment (include photonic streaking) as reviewer #1 commented. Water window HHG has been demonstrated for many years, but no streaking measurements at 300 eV have ever been achieved until this work. We have solved the long-standing issue of character attosecond pulses by photoelectron streaking at high photon energy range.

• Opt Lett 18, 5383 (2014) [ICFO team] – Same setup as present manuscript. Spectrum to 400 eV. NEXAFS measurement. Fig 3 same as present Fig. 4a.

Reply 4: Attosecond pulse train instead of isolated pulse were produced, should not be compared directly. (Same as reply 1)

• Nat Commun 6, 6611 (2015) [ICFO team] – Same laser setup as present manuscript. Isolated asec pulses with photonic streaking, 230-300 eV spectrum.

Reply 5: This paper is indeed the first demonstration of isolation water-window attosecond pulse via photonic streaking. However, the photon flux is not given.

In summary, what is new here is the measurement of the pulse duration of 53 asec. All other parts have been done previously at either UCF or ICFO.

Reply 6:

Our work has solved the long standing difficulties in generating and characterizing isolated attosecond pulses in the 100---300 eV range. Although the generation (polarization gating) and PROOF techniques have been used for 800 nm driving lasers, whether they could be applied to high energy broadband attosecond pulses was uncertain until our work. We demonstrated that nearly 50 as x-ray pulses covering water window could be generated with photon flux high enough for a photoelectron streaking measurement (for the first time). Excellent signal to noise ratio was achieved at the K-edge of carbon for gas samples (figure 4 add in the main text), which paved the road for investigating chemical reaction dynamics using the timed resolved X-ray Absorption Near Edge Spectroscopy (XANES).

Reviewer #3 (Remarks to the Author):

The manuscript by Jie Li et al., entitled as "53-Attosecond X-ray Pulses Glancing Through the Water Window," describes the generation of isolated attosecond pulses in the soft x-ray region, of which the spectrum is extended beyond the carbon K edge, the entrance of the water window (284 - 530 eV).
At UCF, the authors succeed in measuring attosecond spectrograms, which are analyzed by the PROOF method. The spectrograms obtained with Sn filters of different thickness analyzed by the PROOF confirm the effect of filter dispersion and, using a 400-nm-thick Sn filter, the authors confirm the generation of 53-attosecond pulses in the soft x-ray region, which are the shortest light pulses in the world. The results shown in Figs 1 - 3 together with the supplemental information are excellent and worth publishing in Nature Communications.

However, the experimental result (Fig. 4) at ICFO and its interpretation are not convincing. The authors claim the generation of "isolated attosecond" pulses from the streaking spectrogram shown in Fig. 4b. However, the authors do not retrieve the spectrogram to obtain the temporal information of the soft x-ray pulses. Without the pulse duration of the soft x-ray bursts specified, it is inappropriate to use the term "attosecond". Additionally, concerning the term "isolated", the experimental results shown in the manuscript is not enough to claim the isolation of a soft x-ray burst. Please provide CEP dependence of streaking spectrograms and/or high harmonic spectra to estimate the intensity contrast between the primary and satellite pulses.
In summary, the authors are suggested to provide a major revision including additional experimental results to support their claims, modification the interpretation of the experimental results at ICFO, or the removal of the streaking results at ICFO from the manuscript before resubmission for publication.

Reply: We agree with the reviewer and removed the experiment results of ICFO.

===== END OF COMMENTS ==========

REVIEWERS' COMMENTS:

Reviewer #3 (Remarks to the Author, based on the previous comments of Reviewer #1 and the authors' previous response):

Overall, the responses from the authors on the comments 1 - 4 raised by the Reviewer 1 are fine enough so that they would convince the Reviewer 1. The comments 1, 3, and 4 deal with non-technical issues and are responded well. The comment 2 about the photon flux is a technical issue. Although I cannot guarantee validity of the estimated photon flux because a measurement procedure is not well described, the photon flux is not an essential part of the work and the Reviewer 1 also indicated so in the comment 2 as "It would also be helpful to estimate the photon flux above 284 eV.". I would guess the photon flux of their beamline is quite high as they claimed, because they are able to achieve time-resolved soft-x-ray photoelectron spectroscopy, detection efficiency of which is usually lower than direct photon detection. Time-resolved measurement has been highly demanded in the ultrafast community and their achievement is impressive.

Please find below my concerns on their policy about the references. In the manuscript's reference, it would be fair to include some of the five references mentioned in the reply 2. Among the five works, only the second reference, "[2016 ICFO] 7.3×107 photons /s @ 280-550 eV, Nature Communications 7, 11493 (2016)," which is self-reference for the group, is included. These works are closely related to the present work, but not referenced well.

Reviewer #2 (Remarks to the Author):

The major change made to the manuscript was to remove the material from ICFO. Although I feel sorry for the ICFO team, I think that this has made the manuscript more coherent. Also new to the revised manuscript is the demonstration of carbon K-shell photoabsorption at 290 eV. This demonstrates that the attosecond source has sufficient flux at the carbon K-edge for spectroscopy experiments.

The manuscript continues to report mostly technological improvements on attosecond sources, which would be more appropriate for Optics Letters. However the other referees seem to lean towards acceptance by Nature Communications, and I will not block it.

(1) The claim of "water window" still seems a stretch, given that the water window is 280- 540 eV. The spectra shown in Fig. 3 peak at 180 eV, with a tail barely reaching the carbon K-edge. Perhaps the claim could be "reaching the carbon K-edge".

(2) The conclusion now includes a suggestion that a 50 attosecond source would give better time resolution for transient absorption experiments. I am not sure about this claim. Since transient absorption involves the creation of an electronic coherence that persists for a time much longer than the excitation pulse, it is not clear how a 50 asec time resolution will be obtained. For example, the absorption line widths shown in Fig. 4 correspond to an emission time in the femtosecond range.

(3) The pulse duration of the spectral portion above 250 eV is unlikely to be near 50 asec, given the measured spectral phase.

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An absorption measurement is added in Fig.4, which is a currently hot topics in ultrafast laser community when it is combined with time-resolved measurement. In this context, the authors may add an article "Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction," by A. R. Attar from Science as a reference.
I believe this manuscript is worth publishing in Nature Communications.

Response to Reviewer's Comments

We would like to thank Reviewers #2 and #3 again for their comments, which have been addressed in detail in this response. The manuscript has been revised accordingly.

Reviewer #1 (Reviewer #3's comments of Reviewer #1 and our responses from previous round)

Overall, the responses from the authors on the comments 1 - 4 raised by the Reviewer 1 are fine enough so that they would convince the Reviewer 1. The comments 1, 3, and 4 deal with non-technical issues and are responded well. The comment 2 about the photon flux is a technical issue. Although I cannot guarantee validity of the estimated photon flux because a measurement procedure is not well described, the photon flux is not an essential part of the work and the Reviewer 1 also indicated so in the comment 2 as "It would also be helpful to estimate the photon flux above 284 eV." I would guess the photon flux of their beamline is quite high as they claimed, because they are able to achieve time-resolved soft-x-ray photoelectron spectroscopy, detection efficiency of which is usually lower than direct photon detection. Time-resolved measurement has been highly demanded in the ultrafast community and their achievement is impressive.

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Reply: we agree with the Reviewer and add the works *"Carrier-envelope phase-dependent high harmonic generation in the water window using few-cycle infrared pulses. Nat. Commun. 5, 3331 (2014)."* and *"Water-window soft x-ray high-harmonic generation up to the nitrogen K-edge driven by a kHz, 2.1 µm OPCPA source. J. Phys. B: At. Mol. Phys. 49, 155601 (2016)"* as reference # 16 & 17 in second paragraph of the manuscript:

"Recent development of carrier-envelope phase-stabilized few-cycle lasers at 1.6 to 2.1 µm paved the way for the next generation of attosecond light sources. Carrier-envelope phase (CEP)-controlled, soft X-ray pulses reaching the water-window (284-530 eV) have been generated using these driving lasers [16, 17], and evidence of IAPs therefrom were demonstrated [18-20]."

Reviewer #2 (Remarks to the Author):

The major change made to the manuscript was to remove the material from ICFO. Although I feel sorry for the ICFO team, I think that this has made the manuscript more coherent. Also new to the revised manuscript is the demonstration of carbon K-shell photoabsorption at 290 eV. This demonstrates that the attosecond source has sufficient flux at the carbon K-edge for spectroscopy experiments.

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Reply 1: we agree with the reviewer and change the title to "53-Attosecond X-ray Pulses Reach the Carbon K-edge". The word "water window" is also change to "carbon K-absorption edge" in the abstract:

"Here we demonstrate a soft X-ray pulse duration of 53 as and single pulse streaking reaching the carbon K-absorption edge (284 eV) by utilizing intense two-cycle driving pulses near 1.8-μm center wavelength."

(2) The conclusion now includes a suggestion that a 50 attosecond source would give better time resolution for transient absorption experiments. I am not sure about this claim. Since transient absorption involves the creation of an electronic coherence that persists for a time much longer than the excitation pulse, it is not clear how a 50 asec time resolution will be obtained. For example, the absorption line widths shown in Fig. 4 correspond to an emission time in the femtosecond range.

Reply 2: The absorption line width in Fig. 4 is determined by electron state lifetime, which is indeed in femtosecond range. However, in an attosecond transient absorption experiment, we are interested in the changes of such absorption line, such as the changes in its width, position and intensity, which only depend on the time scale of the physical processes that are initiated by an additional pump laser. Therefore, the time resolution of such measurement can be as high as 50 attosecond using our source. Furthermore, X-ray pulses may be absorbed by a group of states in transient absorption that leads to the formation of electronic wavepackets. The energy range of these states may be so large that 50 as pulses are needed to cover them and assure the synchronization of their excitations.

(3) The pulse duration of the spectral portion above 250 eV is unlikely to be near 50 asec, given the measured spectral phase.

Reply 3: As we already stated in the original manuscript, "only the spectral phase error in the low-energy part (<200 eV) of the tin filter transmission window can be well-compensated because the filter's group delay dispersion approaches zero at 300 eV". The achieved 50 asec pulses consist the entire bandwidth and spectral phase. If the spectral phase above 300 eV can be further compensated, a pulse duration less than 50 asec can be achieved.

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The manuscript by Jie Li et al., entitled as "53-Attosecond X-ray Pulses Glancing Through the Water Window," describes the generation of isolated attosecond pulses in the soft x-ray region. The authors succeed in retrieving isolated attosecond pulses from measured attosecond spectrograms using the PROOF method. The spectral range of the photoelectron spectra reach the carbon K edge at 284 eV, the entrance of the water window (284 - 530 eV), for the first time. The spectrograms obtained with Sn filters with the different thicknesses confirm the effect of filter dispersion and, using a 400-nm-thick Sn filter, the authors realize the measurement of 53-attosecond pulses, which are the shortest light pulses in the world. The results shown in Figs 1 - 3 together with the supplemental information are convincing, novel and excellent.
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I believe this manuscript is worth publishing in Nature Communications.

Reply: we added the work "Femtosecond x-ray spectroscopy of an electrocyclic ring-opening reaction" as reference # 29 after Fig.4.

"Charge migration, a process strongly affecting chemical reactivity, occurs on sub to few femtosecond time scale [28, 29]."