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Attosecond circular-dichroism chronoscopy of electron vortices

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ABSTRACT

Circular dichroism (CD) describes the different responses of a chiral object to circularly polarized light of opposite handedness and serves the basis of most chirality-sensitive spectroscopy techniques. All previously observed CD effects originate from the chiral sensitivity of the amplitudes of electron transitions. In contrast, CD effects in the phase of the electron transitions have barely been studied, even theoretically. Here, we present a combined experimental and theoretical investigation of the amplitude- and phase-resolved CDs of continuum-continuum transitions for electron vortices. We employ a circularly polarized attosecond pulse train to prepare electron vortices in the continuum, and a circularly polarized near-infrared laser pulse to probe the chirality of the electron vortices. Our complete experimental reconstruction of the partial-wave amplitudes and phases demonstrates that the photoionization time delay of the continuum-continuum transition depends not only on the angular-momentum quantum number l of the populated continuum state but also on its magnetic quantum number m. Our work defines a general technique called attosecond circular-dichroism chronoscopy (ACDC), which can provide new insights into electron-vortex beams, chiral molecules and magnetic materials on the most fundamental time scales.

Chirality is a fundamental property of asymmetric objects that are abundant in nature, ranging from spiral galaxies over human hands to chiral molecules. In a conventional view, chirality originates in the structure of objects. For example, the nuclear configuration of chiral molecules imposes the chirality onto the electronic spatial distribution, which results in chiral light-molecule interactions. Electron vortices[1] (also called electron ring currents in the case of bound states) are a paradigmatic example of a class of objects for which the chirality originates from their phase structure. Due to the quantization of angular momentum, a freely moving or bound electron may have a nonzero projection of its orbital angular momentum on the quantization axis. This nonzero longitudinal angular momentum $m\hbar$ dictates the electronic helical phase $e^{im\phi}$ spiralling about the quantization axis, where m is the magnetic quantum number and ϕ is the azimuthal angle. Such an electron vortex or electron ring current has naturally attracted much interest[2–10] due to its chiral phase structure. For example, an unusual kind of Ramsey interference between photoelectron wave packets produced by a pair of time-delayed, counter-rotating circularly polarized, attosecond pulses was investigated theoretically[2,3] and then confirmed experimentally[4,5] in multiphoton ionization regime using visible light pulses. The electron vortices have also been exploited in electron-energy-loss spectroscopy of magnetic materials[11] and the electronic spin polarization from atoms[12]. Although the Ramsey interference between electron vortices can probe their helical phases, their attosecond chiral dynamics interacting with lights have so far escaped scrutiny in experiments as a consequence of the shortage of circularly polarized attosecond extreme-ultraviolet (XUV) pulses[13–16] and suitable attosecond metrology in circular polarization.

Chiral recognition of molecules is an important topic in biochemical science, and most of the related techniques are based on the interactions with circularly polarized light (CPL). For example, in traditional CD spectroscopy of chiral molecules, the asymmetry in the absorption of right versus left CPL is typically less than 10^{-3}, since it is dictated by magnetic-dipole transitions. Recently, several techniques of higher selectivity based on the intense electric-dipole transitions have been developed, such as laser-induced mass spectrometry[17], Coulomb-explosion imaging[18,19], photoelectron circular dichroism[20,21] and high-order harmonic spectroscopy[22,23]. Some of them can increase the CD signal beyond 10%. However, all of these chiroptical techniques are based on the amplitude of real-valued electronic-transition dipoles, such that possible CDs in the transition phase have not been considered. With the development of ultrafast science into the attosecond domain[24], the phase information of electronic transitions has become accessible by attosecond metrology, including the attosecond streak camera[25,26] and the reconstruction of attosecond beating by interference of two-photon transitions[27–29] (RABBIT). After determining both the amplitude and the phase of electronic transitions, it can be regarded as a "complete" measurement.

In a recent advance, we established attosecond metrology in circular polarization and demonstrated a plug-in

apparatus to simplify the generation of CPL attosecond XUV pulses based on the non-collinear high-order harmonic generation (HHG) process[15,16]. Here, we employ this metrology to study and manipulate the chiral dynamics of electron vortices on attosecond time scales. A circularly polarized attosecond pulse train is used to photoionize argon atoms, preparing electron vortices with well-defined helicity in the continuum state. We then probe the electron vortices with a synchronized co-rotating or counter-rotating near-infrared (IR) laser pulse through circular-RABBIT measurements. We observe that the sideband (SB) yield in the co-rotating geometry is remarkably enhanced compared with that in the counter-rotating case with a CD signal ranging up to 35%. More importantly, when switching the helicity of the IR probe, we demonstrate that the phase of the SB photoelectrons has dichroic structures and opposite bending directions along the photoemission angle with respect to the light propagation direction, and the corresponding two-photon (XUV+IR) photoionization time delays can differ by several hundreds of attoseconds. Our findings are supported by solving the time-dependent Schrödinger equation (TDSE) in three dimensions. The insights gained from the calculation are then used to retrieve a complete set of partial-wave amplitudes and phases from the experimental data, enabling to separate the phase into the bound-continuum and continuum-continuum transitions and then extract the CD of the continuum-continuum transition phases. Our study provides a quantum-mechanically complete description of the photoionization and continuum dynamics.

In our experiments, the circularly polarized attosecond XUV pulses were generated through HHG in xenon atoms driven by two non-collinear counter-rotating circularly polarized IR (800 nm) beams using a compact beam-in-beam setup. The XUV spectrum contained the odd-order harmonics from H9 (13.95 eV) to H15 (23.25 eV). The weak probing IR field was tuned to be circularly polarized with the same or the opposite helicities with respect to that of XUV. The XUV and IR pulses were spatiotemporally overlapped and then focused onto a thin supersonic beam of argon, and the three-dimensional momenta of the ionized electrons and ions were measured in coincidence using a COLTRIMS (Cold target recoil ion momentum spectroscopy) spectrometer[30,31]. The XUV-IR phase delay was actively stabilized during measurements with a continuous-wave (cw) HeNe laser to a temporal stability of better than 30 as[32]. Our experimental setup is illustrated in the extended-data Figure 5 and more details are given in the Methods section.

Figure 1a illustrates the coordinate system used throughout this work, in which the light co-polarization plane is the x-y plane and the light propagation direction defines the z axis. The outermost valence shell of argon atoms is 3p which consists of three degenerate orbitals, i.e., p_+ (left helicity), p_- (right helicity) and p_0, where the quantization axis of the atomic orbitals is the z axis. Note that in previous RABBIT experiments with linearly polarized lights the quantization axis is usually chosen to be the polarization direction. Our left circularly polarized XUV field will

preferentially ionize the co-rotating orbital, i.e., the p_+, forming an electron-vortex continuum state with $m = 2$. In the extended-data Fig. 6, we show the calculated ionization cross sections and the photoelectron angular distributions from the degenerate 3p orbitals, which confirms the dominance of ionization from p_+. In the light polarization plane, the photoelectron momentum distributions are isotropic and form a doughnut shape due to the circular polarization of both light fields. Since the net angular momentum direction of the electron vortices and the spin angular momentum direction of the probe light are both along the z axis, the chirality must manifest itself in the θ-resolved photoelectron angular distribution, where θ is the photoelectron emission angle with respect to the light propagation direction.

Figures 1b-d show the measured angle-resolved photoelectron energy spectra in the XUV-only, co-rotating, and counter-rotating cases, respectively. The photoelectron emission angle in the polarization plane $\phi = \arctan(p_y/p_x)$ was integrated over its 2π range and the XUV-IR delay was integrated over two IR optical-cycle periods. We observe three main peaks of the electron vortices corresponding to the photoionization by H11, H13 and H15 in the XUV-only case, and two sidebands (SB12 and SB14) after introducing the probe light. The sidebands are formed by the interference between the electronic wavepacket that absorbed one IR photon from the lower main peak and that released one IR photon from the higher main peak. Our experiment shows that the SB yield is remarkably enhanced in the co-rotating case compared to the counter-rotating case, which directly manifests the CD effect on the amplitude of the continuum-continuum transitions of the electron vortices. In Fig. 1e, we illustrate the photoelectron-energy and CD spectra at the angle of 90°, i.e., the co-polarization plane, which has the highest counts and experimental resolution. The energy-dependent CD is defined as $[Y_{\mathbf{co}}(E_k) - Y_{\mathbf{counter}}(E_k)]/[Y_{\mathbf{co}}(E_k) + Y_{\mathbf{counter}}(E_k)]$, where $Y_{\mathbf{co}}(E_k)$ and $Y_{\mathbf{counter}}(E_k)$ are the normalized photoelectron counts in the co- and counter-rotating cases, respectively. Our experimental result demonstrates that the CD signals of SB12 and SB14 can reach up to 35% and 30%, respectively, which is arguably a huge CD signal compared to the previous chiroptical methods. Note that the CD signal is negative at the main peaks because of the depletion effect of the continuum-continuum transitions. Our experiment reveals a basic rule in the electron-photon chiral interaction that the electron vortex prefers to absorb or release a co-rotating photon, which is opposite to a previous experimental observation[33] where the sideband in the counter-rotating configuration was reported to be dominant. In the Methods section, we provide an analytical perspective of the amplitude CD to support our conclusion.

When varying the XUV-IR delay, the angle-resolved sideband yield oscillates with a period of 2ω (ω is the IR center frequency) due to the pathway interference, and the phase of the yield oscillation (also called RABBIT phase) contains the attochirp of the XUV field and the phases of electronic two-step transitions in the ionization process. Here we focus on the angle-resolved RABBIT phase within one sideband and therefore the XUV attochirp

which only depends on the photon energy can be ruled out. In Figs. 1f-g, we show the delay-resolved photoelectron angular distributions of SB12 in co- and counter-rotating geometries, respectively, where the photoelectron energy is integrated over [2.4, 3.2] eV and the photoelectron emission angle in the polarization plane ϕ is fixed at 90°. Our experimental result illustrates the fact that the photoelectrons emitted along different angles with respect to the light propagation direction show different phases for the yield oscillation. Performing Fourier transformation along the axis of the XUV-IR delay, we extract the angle-dependent RABBIT phases for the two geometries, as illustrated in Fig. 1h, and for clarity we add these RABBIT-phase curves onto the two-dimensional RABBIT trace plots in Figs. 1f-g with dashed lines. The RABBIT phase displays the opposite bending directions for the two geometries. For the co-rotating geometry, the photoelectrons emitted closer to the light propagation direction are delayed in time. In contrast, for the counter-rotating geometry the photoelectrons emitted close to 0° or 180° are mostly advanced temporally compared to those emitted in the light-polarization plane. More importantly, by simply switching the IR helicity, the photoionization time delay of the continuum-continuum transition can be tuned on the attosecond timescale. For the photoelectrons emitted in the light polarization plane, the CD effect on the photoionization time delay is about 100 as and it increases to several hundreds of attoseconds for the photoelectrons emitted along the light propagation direction.

To validate our findings, we resort to solving the three-dimensional (3D) TDSE[34] using an effective potential for argon. In the calculation, we considered the three 3p orbitals [p_+ (left helicity), p_- (right helicity) and p_0]. The calculations confirmed that the ionization from p_+ contributes 70% of the total cross section, largely exceeding those from the other two orbitals. More details about the TDSE simulations are given in the Methods section. In Figs. 2a-b we illustrate the simulated delay-integrated angle-resolved photoelectron spectra for the two geometries, and in Fig. 2c we show the photoelectron-energy and the corresponding CD spectra in the light-polarization plane. Note that these results are averaged over the three 3p orbitals. The TDSE simulation predicts that the CD signal could reach 43% for SB12 and 30% for SB14, which agrees with our observations in a reasonable range considering the assumptions made in the TSDE calculations, e.g. the equal intensities for each harmonic order. The angle-resolved RABBIT traces of SB12 in the two geometries and the extracted RABBIT phases are illustrated in Figs. 2d-f, respectively. It is clear that these two kinds of probes cause the opposite bending directions for the phase of the emitted photoelectrons, and the bending degree of the phase in the counter-rotating case is larger than that in the co-rotating case. These orbital-averaged results qualitatively agree with our experiment.

In Figs. 2g-i, we illustrate the corresponding simulation results from the dominant orbital, i.e., p_+. The basic structures of the RABBIT phases are not changed but their curvatures are obviously increased. In the counter-rotating

case, there is a π-shift between the emissions in the polarization plane and along the light propagation direction, which gives rise to the relatively larger bending of the counter-rotating phase in the orbital-averaged result. In the extended-data Fig. 7, we illustrate the RABBIT traces from p_- and p_0 orbitals in the two geometries. There is no CD effect for the ionization from the p_- orbital, since the accessed electronic continuum has $m = 0$, i.e. no chirality. Ionization from the p_0 orbital has similar CD effects in the sideband yield and phase, but the CD degree is smaller compared to the case of p_+ due to the smaller m-value of the electron vortices. The sensitivity of the phase CD to the properties of the initial state demonstrates that our ACDC technique is a sensitive probe of the orbital structure of the ionized target. This conclusion is additionally confirmed by the calculated ACDC effect in He, shown in extended-data Fig. 8.

Figure 3a and c show energy-level diagrams based on ionization from the p_+ ground-state orbital that rationalize the experimental observations on different RABBIT phases for the two different probes. The atomic eigenstates are labeled with the usual atomic physics notation, i.e., with the orbital angular momentum labeled as s ($l = 0$), p ($l = 1$), d ($l = 2$), and f ($l = 3$) followed by its projection (m) on the light propagation direction. An electric-dipole transition changes l by ± 1, and m increases by 1 after absorbing a left-circular photon or releasing a right-circular photon. Satisfying the selection rules of both l and m, in the co-rotating case the upward pathway from the lower main peak creates a pure f3 wave and the downward pathway from the higher main peak forms a mixed wave consisting of p1 and f1. For the counter-rotating case, the populated states are the same as those in the co-rotating case. This naturally raises the interesting question what causes the CD effect on the RABBIT phase. The ratios of p1 and f1 waves in the two geometries are significantly different. Due to the Fano's propensity rule[35,36], i.e., absorbing (releasing) a photon prefers to change l by +1 (-1). Thus, the sideband in the co-rotating case is dominated by the interference of f3 and p1. In contrast, in the counter-rotating case, the sideband is dominated by the interference of f3 and f1. In Figs. 3b and d, we show the interference pattern between f3 and p1 and that between f3 and f1, respectively, assuming equal partial-wave phases and amplitudes. For the co-rotating case the interference between f3 and p1 gives rise to the isotropic phase profile, and the interference between f3 and f1 for the counter-rotating case reproduces the π-shift structure in the RABBIT phase (as visualized by the dashed lines in panels b and d), which actually originates from the alternating sign of the three lobes of the f1 wave. Note that here the goal of this simple two-wave interference model is not a quantitative reproduction of the RABBIT phase, but to illustrate the most fundamental CD effects in the RABBIT phase.

After considering the amplitudes and phases of all participating partial waves, one can fully reproduce the RABBIT traces illustrated in Figs. 2g-i. The TDSE simulation naturally provides this information by expanding

the final wavefunction into a spherical-harmonic basis. Figures 4a-b show the calculated amplitudes and phases of the f3, p1, and f1 partial waves from the p_+ ground-state orbital in the co-rotating and counter-rotating geometries, respectively. In the co-rotating case, the relative amplitude ratio of these partial waves agrees well with Fano's propensity rule, i.e., the p1 wave is dominant over the f1 wave. However, in the counter-rotating case Fano's propensity rule is not entirely correct[37], although the proportion of the f1 wave has obviously increased, which is enough to cause the significant variation in the RABBIT phase. In contrast, the partial-wave phases provide a unique view to the photoionization dynamics of electron vortices. The phase of the f3 wave in the co-rotating case is equal to that of the f1 wave in the counter-rotating case, and similarly the phase of the co-rotating f1 wave is equal to that of the counter-rotating f3 wave. This is because the phase of the electric dipole transition depends on l and the energies of initial and final states for the same azimuthal angle ϕ. The phase of the p1 wave is different in the two geometries since the energies of their initial and final states are different. Therefore, the helicity of the probe light can affect not only the amplitudes of the populated partial waves, but also their phases.

The time- and angle-resolved RABBIT trace is a photoelectron interferogram of partial waves with specific amplitudes and phases, which provides an opportunity of completely recontructing the time-dependent electronic superposition state by using global fittings[38]. Importantly, the photoelectron yield in the angular range from $\theta = 60^\circ$ to $\theta = 120^\circ$ is dominated by ionization from the p_+ ground state, as illustrated in the extended-data Fig. 6d. This allows us to perform the global fitting based on the three-wave interference formula $W_{\mathbf{co}}(\theta,\tau) = |a*f_3(\theta)e^{i(\omega\tau-\phi_a)} + b*f_1(\theta)e^{-i(\omega\tau-\phi_b)} + c*p_1(\theta)e^{-i(\omega\tau-\phi_c)}|^2$ for the co-rotating case and $W_{\mathbf{counter}}(\theta,\tau) = |a*f_3(\theta)e^{-i(\omega\tau-\phi_a)} + b*f_1(\theta)e^{i(\omega\tau-\phi_b)} + c*p_1(\theta)e^{i(\omega\tau-\phi_c)}|^2$ for the counter-rotating case. A fit of this model is shown and compared with the measured interferograms in the extended-data Fig. 9, where good agreement is achieved. The six fitting parameters (a,b,c,ϕ_a,ϕ_b,ϕ_c) are illustrated in Figs. 4c and d for the two geometries. Our retrieved results, especially for the phases, agree well with the values extracted from the TDSE simulation within the fitting uncertainty, validating the CD effect on the transition-matrix phase of electron vortices. Because here the extracted partial-wave phases can be expressed as the sum of the phases from the two steps, i.e. the Wigner phase and the continuum-continuum phase, the phase CD between the two geometries will cancel out the Wigner phase and thus undoubtedly reveals the chirality of the continuum-continuum transition.

Previous experiments[36,38,39] have demonstrated that photoionization time delays depend on the energies and angular momenta (l) of both initial and final states in electronic transitions. Limited by the shortage of circularly polarized attosecond light pulses, the dependence of photoionization time delays on the magnetic quantum number (m) or the light helicity has not been identified prior to this work. The magnetic quantum number fundamentally

defines the spatial orientation and handedness of electronic wavefunctions, which plays an essential role in chiral[40] and topological[41] systems at the frontier of science. For atomic cases studied in this manuscript, the amplitude of the electron vortices does not depend on the ϕ angle, and therefore the atomic electron vortices can be intuitively depicted as a doughnut shape. As for molecular systems, the wavefunction of the electron vortices has some structural/amplitude features depending on the ϕ angle. The spiral phase distribution ($e^{im\phi}$) of each partial wave in molecular vortices is, however, similar to the atomic case. Therefore, the ACDC effect of molecular vortices between co-rotating and counter-rotating IR probes is expected to exist. The ACDC of molecular vortices will depend on not only the θ angle but also on the ϕ angle and the orientation of molecules, providing a sensitive probe to the molecular structural and dynamical information. As a further opportunity, with the development of attosecond light source extending into the XUV and soft-X-ray regimes, inner-shell element-specific attosecond experiments have become possible. With such circularly polarized sources, the prepared electron vortices from molecular inner shells immediately after ionization will be very close to the atomic case, which offers the possibility of using ACDC to probe the effect of electron-vortex scattering in the molecular potential on attosecond time scales.

In summary, we have demonstrated a new technique, attosecond circular-dichroism chronoscopy. We have applied it to the complete measurement of chiral electron-photon interactions, highlighting very large CDs in both amplitude and phase. This technique in the attosecond toolbox can be applied to many other systems such as chiral molecules and topological materials. Photoelectron circular dichroism (PECD) of chiral molecules manifests itself as an amplitude asymmetry in electric-dipole transitions between forward and backward photoemission directions. The forward-backward transition-phase asymmetry has not yet been revealed, although one experiment[42] using femtosecond two-color fields was reported in the strong-field regime, where the results are known to depend on the intensity of the driving fields[43]. ACDC will enable such attosecond experiments on chiral molecules in the perturbative regime, where the results do not depend on intensity and thus reflect the inherent chiral properties of the native systems. Looking further ahead, the full exploitation of electron-ion coincidence measurements or the combination with laser-induced molecular-alignment techniques, will additionally give access to the phase asymmetry of PECD in the molecular frame, defining fully differential attosecond time-resolved chiral chronoscopy.

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Author Contributions Statement

M.H. performed the experiments with the support of J.J. and T. B.. M.H. and H.J.W. analyzed and interpreted the data. Simulations were implemented by M.H.. H.J.W. conceived the study and supervised its realization. All authors discussed the results and wrote the paper.

Competing Interests Statement

All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report.

Figure Legends/Captions

Figure1: Experimental results of the CD effects on continuum-continuum transitions of the electron vortex. **a**, Schematic illustration of the attosecond circular-dichroism chronoscopy experiment. The electron vortex (donut shape with spiral phase distribution) created by photoionization of a left circularly polarized XUV field (purple arrow) is probed by a co-rotating (red arrow) or counter-rotating (blue arrow) IR field. **b**, Measured angle-resolved photoelectron energy spectrum in the XUV-only case. **c, d**, Measured delay-integrated angle-resolved photoelectron energy spectrum after adding a co-rotating (c) and counter-rotating (d) IR field, respectively. In b-d, the photoelectron emission angle in the co-polarization plane, i.e., ϕ=arctan(p_y/p_x), was integrated from 0 to 2π. **e**, Measured photoelectron energy spectra and the corresponding CD spectrum in the polarization plane, i.e., θ=arccos($p_z/p_{\mathbf{total}}$) = 90°. **f, g**, Measured delay- and angle-resolved photoelectron distributions of SB12 in the co-rotating (f) and counter-rotating (g) cases. **h**, Extracted angle-resolved RABBIT phases from f and g using Fourier transformation. The uncertainty (shade area) is estimated by the B/A approach[44]. These two RABBIT-phase curves are also plotted in f and g with dashed lines.

Figure2: TDSE simulations. **a, b**, TDSE simulations of the delay-integrated angle-resolved photoelectron energy spectra in the co-rotating (a) and counter-rotating (b) geometries. **c**, Photoelectron energy spectra and the corresponding CD spectrum in the light polarization plane. **d, e**, Delay- and angle-resolved photoelectron spectra of sideband 12 in the co-rotating (d) and counter-rotating (e) geometries. **f**, Extracted angle-resolved RABBIT phases from d and e. Note that in a-f the results are averaged over the photoelectron momentum distributions from the degenerate p_+, p_- and p_0 orbitals. **g-i**, The corresponding results from the p_+ orbital alone.

Figure3: Interference mechanism in co-rotating and counter-rotating geometries based on the p_+ ground state. **a, c**, Energy-level diagrams for the co-rotating probe (a) and the counter-rotating probe (c). The dominant contributions according to Fano's propensity rule are labeled with bold letters. **b, d**, Simplified two-wave interference

pattern between f3 and p1 for the co-rotating case (b), and that between f3 and f1 for the counter-rotating case (d). In b and d, the dashed curves depict the extracted RABBIT phases.

Figure4: Amplitude and phase of the relevant partial waves at sideband 12. **a, b**, TDSE Results from the p_+ ground-state orbital for the co-rotating and counter-rotating geometries, respectively. **c, d**, Global-fitting results of the experimental data for the two polarization configurations. Note that the amplitudes are normalized to the sum in each case. The error bars and the shaded areas in c and d represent the 95% confidence intervals for the fitting parameters obtained by nonlinear regression.

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Methods

Experimental details. Our experimental setup is illustrated in the extended-data Fig. 5. Near-infrared laser pulses (2 mJ) were delivered from a regenerative Ti:sapphire laser amplifier at a central wavelength of 800 nm with the repetition rate of 5 kHz. A pulse duration of 25 fs for the full width of half maximum in intensity was measured by a home-built FROG apparatus. This laser beam was split with a 70:30 beam splitter, and the more intense part was sent through our beam-in-beam module and then focused by a silver mirror (f = 35 cm) into a 4 mm long, xenon-filled gas cell to generate a circularly polarized extreme-ultraviolet attosecond pulse train via high-harmonic generation. Our beam-in-beam module consists of a specially designed half waveplate and a common quarter waveplate. The half waveplate is composed of two half disks and the relative angle between the fast axes of the two parts is 45°. For example, in our case the fast axes are oriented at $\pm 22.5^\circ$ with respect to the horizontal boundary, respectively. After passing through this half waveplate, the polarization directions of the upper part and the bottom part of the beam are orthogonal to each other. The two parts of the beam are then converted to be circularly polarized but with opposite helicities by transmission through the quarter waveplate. The left-circularly polarized XUV beam in the two produced beams was picked up using a perforated mirror and focused into the main chamber of a COLTRIMS by a nickel-coated toroidal mirror (f = 50 cm). The XUV spectrum was characterized with a home-built XUV spectrometer consisting of an aberration-corrected flat-field grating (Shimadzu 1200 lines/mm) and a micro-channel-plate (MCP) detector coupled to a phosphor screen. We completely characterized the Stokes parameters and the temporal structure of our XUV pulses. In the attosecond pulse train, the duration of each of the composite attopulses was measured as ~ 940 as for the amplitude FWHM, corresponding to 480 as for the intensity FWHM. The ellipticities of the harmonics are 0.98, 0.94 and 0.87 for H11, H13 and H15, respectively. The IR beam with 30% energy was used as the dressing field in RABBIT experiments. The dressing IR field was adjusted to

left- or right-circular polarization by a zero-order quarter waveplate and its intensity was controlled at a very low level (about 10^{12} W/cm^2) by an iris. The dressing IR beam was focused by a perforated lens (f = 50 cm) and then recombined with the XUV beam by a perforated mirror. In the arm of the dressing field, there were two delay stages, i.e., a high-precision direct-current motor (PI, resolution 100 nm) and a piezoelectric motor (PI, resolution 0.1 nm), adjusting the interpulse delays on femtosecond and attosecond time scales, respectively. A HeNe continuous-wave laser beam was sent through the beam splitter and traced the IR path in the two arms of the interferometer. A fast CCD camera behind the recombination mirror was used to lock the phase delay between the two arms through a PID feedback. When scanning the XUV-IR phase delay in the measurements, the piezo delay stage was actively stabilized at the step size of 156 as with the time jitter of less than 30 as. For the COLTRIMS setup, the supersonic gas jet of argon atoms (backing pressure of 1 bar) was delivered along the x direction by a small nozzle with an opening hole diameter of 30 μm and passed through two conical skimmers (Beam Dynamics) located 10 mm and 30 mm downstream with a diameter of 0.2 mm and 1 mm, respectively. For the COLTRIMS spectrometer, static electric ($\sim$ 2.21 V/cm) and magnetic ($\sim$ 5.92 G) fields were applied along the y axis to collect the charged fragments in coincidence. Only the single ionization (one electron is coincident with one Ar^+) events are presented in this work.

TDSE simulation. We performed the TDSE simulations based on an open-source TDSE solver, Qprop 2.0[34], where the details of the algorithm and the source code are available. In the simulation, we used the model potential $V_{\mathbf{eff}} = -[Z + (Z_{\text{full}} - Z)\exp(-r_s \cdot r)]/r$ within the single-electron-approximation, where $Z = 1$ and $Z_{\mathbf{full}} = 18$ are the asymptotic ion charges as $r \to \infty$ and $r \to 0$, respectively. The screening length $r_s = 0.2149$ is used to match the ionization potential $I_p = 15.6$ eV of argon. The initial magnetic quantum number m was tuned to be 1, 0 and -1 without changing the ionization potential, respectively. The final photoelectron momentum distribution was averaged non-coherently over these three degenerate orbitals. The vector potential of the XUV field is $A_{\mathbf{XUV}}(t) = -A^0_{\mathbf{XUV}} \sum_{i=11,13,15,17} \mathbf{sin}^2(\omega t/2n_c) * [\mathbf{sin}(i\omega t)\vec{x} + \mathbf{cos}(i\omega t)\vec{y}]$ and that of the IR field is $A_{\mathbf{IR}}(t) = -A^0_{\mathbf{IR}} \mathbf{sin}^2(\omega t/2n_c) * [\mathbf{sin}(\omega(t+\tau))\vec{x} + \mathbf{cos}(\omega(t+\tau))\vec{y}]$, where the amplitude $A^0_{\mathbf{XUV}} = 0.00534$ **a.u.**, $A^0_{\mathbf{IR}} = 0.0033$ **a.u.**, the pulse duration amounts to $n_c = 6$ optical cycles, and the XUV-IR delay τ was uniformly sampled by 24 points in one IR cycle. The discretization box used for the simulations had a radial box size of 150 a.u. with the grid size of 0.2 a.u.. The maximum angular momentum included is $l_{\mathbf{max}} = 15$, which is big enough to cover all ionized electronic partial waves. The time step was $\Delta t = 0.04$ a.u.. To avoid unwanted reflections from the boundaries, a complex boundary absorber was placed starting at 100 a.u. before the end of the simulation. The convergence of the numerical calculations has been checked with respect to all discretization parameters. Qprop has two different expansion modes for the finally obtained wavefunction depending on which kinds of physical variables are being extracted. When showing

the calculated angular distribution of photoelectrons, the first expansion mode was used and the Jacobian matrix ($\sin\theta$) was taken into account. The momentum box was set from 0.1 a.u. to 1.1 a.u. with 100 bins, and there are 91 uniform bins for $\phi = \arctan(p_y/p_x)$ in the 2π range and 19 uniform bins for $\theta = \arccos(p_z/p_{\mathbf{total}})$ in the π range. When displaying the calculated amplitudes and phases of all populated partial waves, the second expansion mode was used.

Analytical perspective of the continuum-continuum transition matrix element. Here we consider the helium case which corresponds to the previous study[33]. After absorbing a left CP XUV photon, the electronic state at the main peak is the p_{+1} state. Then absorbing a co-rotating IR photon, the electronic state at the sideband is the d_{+2} state, and the corresponding continuum-continuum transition probability can be expressed as the product of radial and angular integrals, $Y_{\mathrm{co}} = |<\Psi_{\varepsilon d}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2 * |<Y_{22}(\theta,\phi)|Y_{11}(\theta,\phi)|Y_{11}(\theta,\phi)>|^2 = |<\Psi_{\varepsilon d}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2 * \frac{3}{10\pi}$, where the angular integral is calculated using the Gaunt coefficients. In the counter-rotating IR probe, the populated states are d_0 and s states, and the transition probability is $Y_{\mathrm{counter}} = |<\Psi_{\varepsilon d}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2 * \frac{1}{20\pi} + |<\Psi_{\varepsilon s}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2 * \frac{1}{4\pi}$. $Y_{\mathrm{co}} > Y_{\mathrm{counter}}$ gives rise to the condition that $|<\Psi_{\varepsilon d}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2$ is larger than $|<\Psi_{\varepsilon s}(r)|\hat{r}|\Psi_{\varepsilon p}(r)>|^2$, which is exactly the Fano's propensity rule in the continuum-continuum transition (see Fig. 4 in a previous theoretical study[45]) when the photon energy is away from Cooper minimum or autoionization states. Therefore, the total sideband yield in the co-rotating geometry is larger than that in the counter-rotating geometry. In the extended data Fig. 9, we show the TDSE simulations on helium atoms and similar amplitude and phase CDs are validated.

Data availability

Source data are available for this paper. All other data that support the plots within this paper and other findings of this study are available from the corresponding author (M.H.) upon reasonable request.