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Symmetry resolved atomic photoionization phase shift by attosecond coincidence metrology

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Attosecond chronoscopy is central to the understanding of ultrafast electron dynamics from gas to condensed phase with attosecond temporal resolution. It has, however, not yet been able to determine the timing of individual partial waves, and steering their contribution has been a substantial challenge. Here, we develop a polarization-skewed attosecond chronoscopy to reveal their roles from the angle-resolved photoionization phase shifts in rare gas atoms. By scanning the relative polarization angle between an extreme ultraviolet attosecond pulse train and a phase-locked near-infrared laser field serving as a partial wave meter, we break the cylindrical symmetry and observe an emission direction dependent phase shift in the photoionized electron momenta. The experimental observations are well supported by numerical simulations using the R-matrix with time-dependence method, and by analytical analysis using the soft-photon approximation. Our symmetry-resolved, partial-wave analysis identifies the transition rate and phase shifts of each individual ionization pathway in the attosecond photoelectron emission dynamics. Our findings provide critical insights into the ubiquitous attosecond optical timer and the underlying attosecond photoionization dynamics, thereby offer new perspectives for the control, manipulation and exploration of ultrafast electron dynamics in complex systems.

Introduction

Attosecond light pulses permit real-time observation and precise manipulation of ultrafast electron dynamics¹. This ‘attosecond chronoscopy’ includes two main approaches, the frequency-domain technique of the reconstruction of attosecond beating by interference of two-photon transitions (RABBITT) technique^{2,3} and the time domain technique of the attosecond streaking camera^{4,5}. Both techniques have been applied to a wide range of attosecond time-resolved photoelectron emission dynamics in atoms^{6–8}, molecules^{9–11} and even condensed matters^{12–15}. Studies have demonstrated the photoelectron emission time delays arising from different ionization shells^{16–18}, shape resonances^{9,10,19}, electron correlation²⁰, orbital asymmetry²¹, spatial asymmetry (chirality)¹¹, and electron delocalization²². These time delays are attributed to the energy dependence of the scattering phase shift during electron transitions in a short-range potential and the laser field coupling effect in the continuum^{23,24}. The scattering phase shift is generally understood in terms of the Wigner-Smith time delay^{25,26} which provides a good description for single-photon ionization, and is a good approximation at high photon energies and photoelectron kinetic energies^{23,24}. However, at low photoelectron kinetic energies, the photoionization time delay shows a strong dependence on the emission angle, and the two-photon ionization phase shifts and attosecond time delays have not been well characterized.

The angular dependence of ionization processes is expressed through the photoelectron angular distribution (PAD), which acts as an interferogram in connecting the experimental observable with the underlying electron wave-function^{27,28}. The PAD, $I(\theta, \phi)$, may be defined as

$$I(\theta, \phi) \propto \sum_{l=0}^{l_{max}} \sum_{m=-l}^l \beta_{lm} Y_{lm}(\theta, \phi), \quad (1)$$

where the quantization axis is defined by the laser polarization vector, θ and ϕ are the polar and azimuthal angles of photoelectron emission direction, Y_{lm} is the spherical harmonics, and β_{lm} are expansion coefficients. Traditional RABBITT measurements²⁹ using parallel-polarized extreme ultraviolet attosecond pulse trains (XUV-APT) and near infrared (NIR) laser fields report a cylindrically symmetric PAD and a large angle-dependent phase shift, close to π , which is ascribed to the incomplete quantum interference following Fano’s propensity rule^{29–31}. However, as the relative polarization direction between the XUV-APT and NIR is skewed^{32,33}, the symmetry is broken. The induced asymmetry provides an opportunity not only to investigate the two-photon, transition-induced photoionization time delays, but also to resolve the interference between partial waves with different magnetic quantum numbers.

In this work, we employ an advanced attosecond coincidence metrology, where the polarization axes of the XUV-APT and NIR laser pulses are rotated from a parallel to a perpendicular orientation, as illustrated in Fig. 1(a), to serve as a partial wave meter. This polarization-skewed RABBITT scheme allows us to monitor the photoelectron emission dynamics in time and space simultaneously by steering the different partial waves in the final sideband electrons (see the inset of Fig. 1(a)). PADs of argon and neon atoms are measured with an attosecond time-delay axis to reveal the role of symmetry and scattering phase at the instant of photoionization. Significant cylindrical asymmetry is observed both in the PADs and phase shifts as a function of the electron emission angle, θ , and polarization skew angle, Θ_T . *Ab initio* theoretical simulations agree well with the experimental observations and facilitate the resolution of the two-photon transition phase shifts for each partial wave. Symmetry-resolved partial wave analysis demonstrates that each partial wave presents a homogeneous scattering phase shift distribution, and thus that the skewed PADs and cylindrically-asymmetric phase shifts must arise from the interference between different partial waves.

Angle-resolved photoionization time delays

Our experiment employs an advanced attosecond coincidence interferometer constructed by combining the RABBITT attosecond clock² and electron-ion three-dimensional momentum coincidence spectroscopy of COLTRIMS (COLd Target Recoil Ion Momentum Spectroscopy)^{34,35}. The linearly polarized NIR field dresses the continuum electron wave-packet via a two-photon process, as shown in the insets of Fig. 1(a). Absorption of an XUV photon of harmonic order $2n + 1$ or $2n - 1$ is followed by the absorption or emission of an NIR photon. Thus the same final electron energy is accessible by two distinct, two-photon pathways. The XUV-APT, produced via high harmonic generation in a xenon gas filled cartridge^{36,37}, contains harmonics from 11th order (17.16eV) to 17th order (26.52eV) releasing the main bands from M11 to M17 in argon (M15 to M17 in neon). As shown in Fig. 1(b), the electron sidebands, induced by the NIR absorption and emission processes, are labelled as SB12 to SB16 in argon (SB14 and SB16 in neon), respectively. To investigate the complete, angle-resolved photoelectron emission phase shifts, all ionized electrons are accumulated in a single recording window to achieve a 4π solid angle detection. The released photoelectrons are measured as a function of the relative time delay between the phase locked XUV-APT and NIR pulse (see Methods), where the positive time delay means that the XUV-APT arrives after the NIR pulse.

Figure 1(c) shows the measured photoelectron spectra as a function of the relative pump-probe time delay, and Fig. 1(d) shows the measured PADs of neon under different skewed polarizations between XUV-APT and NIR with $\Theta_T = 0^\circ, 54.7^\circ$, and 90° , respectively.. PADs measured for neon and argon for other values of Θ_T are provided in the supplementary material (SM), and are compared to PADs calculated using the R-matrix with time-dependence (RMT) code³⁸. Due to the absorption and emission of an NIR photon from the neighboring main bands, the initial oscillation phase of the sidebands encodes the chirp difference between the neighboring harmonic combs of the XUV-APT, and the photoionization electron transitions and propagation phase shifts of interest as compared to a free electron wavepacket with the same kinetic energy in the continuum. The sideband oscillation can be expressed as a function of the pump-probe time-delay τ , as $S(\tau) \propto A_{2\omega} \cos(2\omega\tau + \phi_0(\theta))$, and the atomic phase shift term $\phi_0(\theta)$ can be further decomposed into $\phi_0(\theta) = \phi_{\text{atom}}^{2hv}(\theta) + \phi_{\text{XUV-APT}}$, where θ is the emission angle of the photoelectrons in y - z plane and only the atomic phase shift term $\phi_{\text{atom}}^{2hv}(\theta)$ has an angular dependence.

To emphasize the angle-resolved phase shifts, we define a new relative phase shift term as $\Delta\phi_{\text{rel}}^{\Theta_T}(\theta) = \phi_0(\theta) - \phi_0(\Theta_T)$, where the chirp difference of XUV-APT ($\phi_{\text{XUV-APT}}$) is automatically canceled out. Figures 2 (a-c) show angle-resolved relative phase shifts $\Delta\phi_{\text{rel}}^{\Theta_T}(\theta)$ of the argon atom with Θ_T set to $0^\circ, 54.7^\circ$ and 90° , respectively. Clear cylindrical symmetry can be observed in the phase shift distributions at $\Theta_T = 0^\circ$ and 90° . The relative phase shifts $\Delta\phi_{\text{rel}}^{\Theta_T}$ drift to π at $\Theta_T = 0^\circ$ along the direction perpendicular to $\theta = \Theta_T$, but keep almost the same value at $\Theta_T = 90^\circ$. As Θ_T is skewed to an arbitrary angle, for example $\Theta_T = 54.7^\circ$, the 180° rotation symmetry is still present, but the cylindrical reflection symmetry is broken. The maximum phase shift difference at arbitrary Θ_T is fixed at π and displays a new rotational symmetry axis with respect to the NIR polarization direction. Figures 2 (d-f) show the same results as Figs. 2 (a-c) but for neon. The relative phase shift $\Delta\phi_{\text{rel}}^{\Theta_T}(\theta)$ of neon is larger than that of argon in the direction perpendicular to $\theta = \Theta_T$ at $\Theta_T = 90^\circ$. (Results for additional Θ_T values are provided in the SM.) Our full quantum simulations, calculated using the RMT code, agree well with the experimental observations.

Symmetry breaking in skewed polarization

To understand the behavior of the observed phase shift steered by the NIR fields, we perform a partial wave analysis of the theoretical simulations. Figure 3 presents the partial-wave-resolved phase shifts, obtained from RMT calculations, for the accessible two-photon channels: $p_{m=0,\pm1}$ and $f_{m=0,\pm1,\pm2,\pm3}$. Our simulation shows that each individual partial- m -wave acquires a unique and

constant scattering phase shift during the photoionization (see SM for more details). The partial- m -waves have the same yield and phase shift for positive and negative sign of m . Thus the variation of the p and f -wave phase shifts with photoelectron emission angle arises from interference between the various partial- m -waves. The f -wave shows a homogeneous distribution for $\Theta_T = 0^\circ$ (Fig. 3 (a)) and small variations for $\Theta_T = 54.7^\circ, 90^\circ$ (Figs. 3 (b-c)). By contrast, the p -wave shows much larger phase shifts, which oppose the total, observed phase shifts.

Figure 4 shows the lm - partial wave resolved ionization yields and scattering phase shifts as a function of rotation angle Θ_T . As the NIR field direction is skewed away from the XUV-APT in Fig. 4 (a), the $p_1 : p_0$ ratio varies only slightly as a function of Θ_T in argon. However the relative ratios between the m -resolved f -wave ionization yields, $f_1 : f_0$ or $f_2 : f_0$, increase dramatically. In contrast to the transition amplitude, the scattering phase shifts, which is defined as η_{lm} , in Figs. 4(c) and (d), remain approximately constant as a function of Θ_T for f -waves, but increase dramatically for p -waves. These phase shifts can be interpreted as the emission delays for each pathway^{25,26} ($\tau = \eta_{lm}/2\omega$), and thus emission of the f -partial-waves is almost synchronized. The maximum phase shift of f_0 and f_1 -wave at $\Theta_T = 54.7^\circ$, $\eta_{f0} - \eta_{f1} = 0.01\pi$, corresponds to a relative emission time delay of approximately 7as. At $\Theta_T = 20^\circ$, the η_{f2} differs from $\eta_{f0,f1}$ corresponding to a relative emission time delay of 22as. As the skew angle Θ_T increases from 20° to 90° , the f_2 -wave tends to emit more synchronously with f_0 and f_1 -wave. The f_3 components arise only from second-order processes, and therefore make a negligible contribution. As illustrated in Fig. 1(a), within the electric dipole approximation, final f -states can only arise from a single pathway, $p \rightarrow d \rightarrow f$. Hence, the ratio between the final magnitudes and the phase shifts of m -resolved f -waves is independent of the atomic structure, and common to both atoms.

The ratio between p and f -waves is constant in argon, but for neon, this value shows a strong Θ_T dependence. Correspondingly, the ratio $p_1 : p_0$ increases in line with the total p -wave yield in neon but is approximately constant in argon. This difference is also manifested in the phase shifts. In argon the p_0 -wave slows down by $0.13\pi(90\text{as})$ moving between $\Theta_T = 0^\circ$ and $\Theta_T = 90^\circ$, whereas in neon the same change in Θ_T causes a significantly larger delay of $0.55\pi(367\text{as})$. The p_1 -wave slows down by $0.05\pi(33\text{as})$ in argon and speeds up by $0.03\pi(20\text{as})$ in neon. As shown in the insets in Fig. 1(a), the final p -states follow two ionization pathways: $p \rightarrow s \rightarrow p$ or $p \rightarrow d \rightarrow p$, and the $p \rightarrow s \rightarrow p$ pathway shows an isotropic Θ_T dependence. The influence of the atomic system on the phase shift difference between p_0 and p_1 is difficult to assess unambiguously. The phase shift difference is influenced by the exact atomic potential changes for argon and neon weighted

with the z operator, the notably different kinetic energies of the photoelectron (argon SB14 $E_e \sim 6.1$ eV, and neon SB16 $E_e \sim 3.6$ eV), and the different populations of s and d -intermediate states during the single XUV photon absorption process (see SM for more details)³⁹. The skewed NIR field causes a (time-dependent) dipole distortion of the atomic potential, which, in its simplest form, is the laser-driven oscillatory motion of the electron cloud. The effect of this motion is a dipole polarization term with overall p -symmetry, which is then probed by the XUV field in the z -direction. Hence the phase will be most affected by the oscillatory motion along the z -direction, and will be affected less along the y -direction, i.e. for perpendicular polarization. Numerically, the dipole transitions are evaluated through the z operator. Hence a stronger p_0 -partial wave rotational angle dependence is observed and a smaller effect is observed for phase shifts for perpendicular polarization, which leads to the suppressed effect in the p_1 -partial wave.

To provide an analytical expression for the Θ_T dependence of these ratios, we use the ‘soft photon approximation’⁴⁰, which states that the S -matrix transition amplitude for the two-photon RABBITT ionization processes takes the form

$$S^{\pm 1} \sim \cos \Theta_T \sum_{l,m} a_{lm} Y_{l,m}(\theta_k, \phi_k) + \sin \Theta_T \sum_{l,m} b_{lm} Y_{l,m}(\theta_k, \phi_k), \quad (2)$$

where $+$ ($-$) denotes the absorption (emission) process, a_{lm} and b_{lm} are complex coefficients that are independent of Θ_T , and are related to dipole transition elements. A simplified expression for the yield of a photoelectron is given as

$$P_{lm} \sim \cos^2 \Theta_T |a_{lm}|^2 + \sin^2 \Theta_T |b_{lm}|^2. \quad (3)$$

Hence, we divide the electron transition process into two steps, and the skewed NIR field introduces a rotated coordinate system Θ_T with respect to the original frame. Therefore, the one-photon, continuum photoelectron wave packet, whether absorbing or emitting one NIR photon, should include full partial wave interference after projection onto the new rotated coordinates. Although the soft-photon approximation is able to predict the weights of the different partial waves reasonably accurately, as shown in Fig. 4, it predicts phase shifts which depend only on the orbital angular momentum l , and not on the magnetic quantum number m . Advanced approaches are required to predict the corresponding changes in the phase shifts for the different partial waves. These phase shifts can be associated with subtle changes in the structure of the bound and continuum atomic states due to the XUV and NIR laser fields, and can form the basis for new types of exploration of atomic and molecular properties in ultrafast laser fields.

Conclusion

In summary, we employed an advanced attosecond coincidence metrology to investigate the atomic phase shift, induced by two-photon ionization, as a function of the photoelectron emission angle in argon and neon. By controlling the relative polarization angle between the XUV-APT and NIR laser pulses, we observe a phase shift close to π in the photoelectron emission direction that is perpendicular to the NIR polarization axis. The asymmetric and skew characteristics in the atomic phase shifts are attributed to the NIR field, which distort the spherical symmetry of the atom at the moment of photoionization. Our quantum RMT calculations and semi-classical, soft photon approximation model agree well with our experimental observations, further demonstrating that the angular variation in phase shifts originates from the quantum interference between m -resolved partial waves. Our findings provide critical insights into the attosecond atomic clock and the underlying time-resolved photoionization dynamics, and also open a pertinent question related to photoionization time delays with skewed polarization. How do the sophisticated two-photon transition elements relate to symmetry breaking in the full atomic system, including the laser field coupling in a long-range Coulomb potential, transitions involving the continuum electron, and the accurate atomic potential which is polarized by the NIR field? Additionally, our experimental methods provide a state-of-the-art approach which can investigate and manipulate symmetry-resolved photoemission dynamics on an attosecond time scale, including shape resonances dominated by high-angular-momentum continuum waves^{9,10,19}, constructive and destructive interference between multiple coupled states⁴¹, and correlated shake-up and shake-off double ionization assisted by Auger decay^{18,20}.

Methods

Attosecond coincidence interferometer The attosecond photoelectron spectra are measured via an attosecond coincidence interferometer^{19,22}. A multipass amplified Titanium-Sapphire laser system which produces a near-infrared (NIR) femtosecond laser pulse with a central wavelength of 790 nm, 1.4 mJ at 10 kHz repetition rate and a pulse duration of 28 fs (full-width at half-maximum in intensity), is used to construct our attosecond optical interferometer through a nonlinear Mach-Zehnder interferometer. The XUV-APT is generated by focusing the NIR pulse into a capillary filled with xenon gas. The generated XUV spectrum is filtered through a coaxial aluminum foil of thickness 200 nm installed on a quartz ring, yielding a final photon energy range from 11th order (HH11, 17.16 eV) to 17th order (HH17, 26.52 eV). The filtered XUV-APT is recombined with the

drumming NIR pulse through a central hole silver mirror. The XUV-APT and NIR laser fields are phase-locked in the time domain and their relative time delay is manipulated via a delay stage with an attosecond time resolution. To achieve an attosecond stability, the nonlinear interferometer is actively stabilized^{17, 19, 22, 42} with a time-jitter around 30 as.

The delay-controlled XUV-APT and NIR were focused onto the supersonic gas jet in the COLTRIMS³⁴. The single photoionization induced ion and electron fragments were guided by a homogeneous electric and magnetic field towards the ion and electron detectors. Their three-dimensional momenta were reconstructed from the positions and times of flight recorded from the detectors, which contain two micro-channel plates (MCP) and delayline anodes. The intensity of the NIR laser field in the interaction range is estimated to be 2×10^{12} W/cm².

Ab initio simulations Theoretical results are obtained using the R-matrix with time-dependence (RMT) code^{38, 43, 44}. The method employs the R-matrix division of space, whereby a small ($20 a_0$), inner region contains the Ar⁺/Ne⁺ ion, coupled to a continuum electron. In this region, full account is taken of electron exchange. In the outer region, we neglect exchange, and a single, ionized electron can propagate far from the residual ion. This permits the tractable solution of the time-dependent Schrödinger equation in each region, and the wavefunction is matched at the boundary. The description of argon and neon used in the calculations follows Ref. ⁴⁵.

To model the RABBITT measurements, the time-varying electric field is treated classically within the dipole approximation. The NIR-pulse is modelled as a 10-cycle, 760 nm pulse, with a peak intensity of 10^{12} W/cm² and 3 cycle $\sin^4$ ramp on/off. This equates to a pulse duration of 25 fs. The XUV-APT has a peak intensity of 10^{10} W/cm² and is constructed to approximate the frequency comb of the experimental XUV-APT. We propagate the wavefunction for a further 12 fs after the end of the pulse, for a total propagation time of 36 fs, allowing the outgoing wave packet to be resolved from the bound-state wavefunction. The ejected electron is described up to a distance of $5160 a_0$ from the nucleus. We calculate the final wavefunction for 16 time-delays spanning a single cycle of the NIR field.

Following time propagation, we obtain the photoelectron momentum distribution in the laser polarization ($y - z$) plane, by decoupling the photoelectron wave-function from that of the residual ion, and transforming into momentum space via a Fourier Transform. This momentum distribution is resolved into the individual partial wave contributions by selecting the requisite l and m of the

outgoing electron. The lm -resolved yields are then obtained by integrating these distributions over the sideband momentum and angular variables.

Analytical analysis of two photon ionization time delays The analytical dependence of the ionization yield on relative polarization angle can be provided by the ‘soft photon approximation’⁴⁰, which provides an expression for the S -matrix transition amplitude for two-photon XUV-NIR processes. The method is based on the strong-field approximation, and the variation with relative polarization angle is extracted through a first-order, time-dependent perturbation approach.

Fig.1: Schematic diagram of attosecond coincidence metrology. (a) Experimental setup. The polarization-skewed XUV-APT and NIR laser fields were focused onto a supersonic gas jet separately. The three-dimensional momenta of the photoionization released ions and electron fragments were measured in coincidence as a function of the APT-NIR pump-probe delay, and the XUV spectrum is characterized via an online soft-X-ray spectrometer. The insets show the quantum transition map leading to the sideband electron, and the lm -resolved electron wavefunctions along the transition pathways, which are quantized along the z -axis. (b) The energy diagram of the photoionization by two neighboring harmonic orders and the creation of the sideband spectrum in neon. (c) The attosecond photoelectron kinetic energy spectrum as a function of APT-NIR pump-probe delay. (d) The measured PADs averaged over pump-probe time delays with a skew angle of $\Theta_T = 0^\circ, 54.7^\circ$ and 90° , respectively. The left-right intensity asymmetry is from the incomplete detection efficiency of the electron detector. 10

Fig.2: Angle-resolved atomic relative phase shift. (a-c) The relative photoelectron phase shift distributions, $\Delta\phi_{\text{rel}}^{\Theta_T}(\theta)$, in units of π radians as a function of the photoelectron emission angle of argon at a skew angle of $\Theta_T =$ (a) 0° , (b) 54.7° and (c) 90° . The circles and solid lines show the experimental and theoretical results, respectively. The shaded area indicates the fitting error uncertainty. (d-f) shows the same as (a-c) but for neon.

Fig.3: Quantum partial wave coherent superposition. (a-c) The l -partial wave resolved photoelectron phase shift distributions of p -wave (dark blue), f -wave (cyan) and their coherent superposition in the final sideband (orange) in argon atom at the skew angle of $\Theta_T =$ (a) 0° , (b) 54.7° and (c) 90° . (d-f) shows results for the same Θ_T values as (a-c) but for neon.

Fig.4: Full partial wave analysis. (a-b) Partial wave proportions (averaged over all pump-probe time delays) as a function of Θ_T in argon (a) and neon (b). The light blue and brown areas show the m integrated proportions of the p -wave and f -wave. Blue squares and red triangles show the p_0/p_1 relative ratio via RMT and SPA simulation, respectively. The yellow dot-line and green triangle-line show the relative portion ratios for f_1/f_0 (dark) and f_2/f_0 (light) via RMT and SPA, respectively. (c-d) The lm -symmetry resolved photoelectron phase shifts in argon (c) and neon (d) calculated using RMT. The phase shifts of p_0 and p_1 electrons are labelled as dark blue and light blue, and phase shifts of f_0 , f_1 and f_2 electrons are shown as dark orange, orange and light orange colors.

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Author Contributions: X. G. and J. W. conceived the idea and initiated the study. X. G., W. J., J. T., and J. W. carried out the experiments and the data analysis. A. B. performed the RMT calculations. G. A. carried out the analytical SPA derivations. X. G., W. J., and G. A. performed the partial wave data analysis. A. B., G. A., D. C. and J. B. developed new capabilities within the RMT code which were used in this work. X. G., W. J., G. A., H. N., H. v.d.H., A. C. B., and J. W. wrote the manuscripts with input from all the authors.

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