

Supplementary Material for Resolving Quantum Interference Black-Box through Attosecond Photoionization Spectroscopy

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The PDF file includes:

Supplementary Text
Figs. S1 to S8

Reconstruction of the sideband phase shifts

Figure S2 displays the sideband reconstruction principle in neon from the experimental measurements at $\Theta_T = 0^\circ$. Figure S2a is the emission angle integrated photoelectron kinetic energy spectrum, the solid line represents the result from multiple Gaussian fitting. We perform a fast Fourier transform (FFT) analysis of the 2-Dimensional RABBITT spectrum shown in Fig.S 2b, the resulting oscillation amplitudes and phase shifts of the $2\omega_{\text{NIR}}$ components are demonstrated in Fig. S2c and d, respectively. Besides, we also perform a global fitting of the measured RABBITT spectrum using the expression:

$$I_{\text{fit}}(E, \tau) = \sum_j a_j e^{-\frac{(E-b_j)^2}{2c_j^2}} \left[\cos(2\omega_{\text{NIR}}\tau + \phi_0) + d_j \right], \quad (1)$$

where j is the number of both the main peaks and sidebands, ϕ_0 for each sideband photoelectron is the oscillation phase results from the sum of the chirp of the XUV-APT, the effective two-photon transition phase including the relative one-photon scattering phase shifts between adjacent high harmonics and the relative continuum-continuum transition phase shifts between emission or absorption pathway (1, 2), and an unknown phase offset due to the onset of the oscillation. Applying the same FFT analysis of the reconstructed 2D RABBITT spectrum, the oscillation phase shift which is displayed by the solid line in Fig. S2d agrees well with the results directly from the experimental measurements. Figure S2e to S2h show the same sideband phase reconstruction at $\Theta_T = 90^\circ$, where the NIR field is polarized perpendicular to the XUV-APT. Figure S3 displays the same results in argon with high harmonic combs from xenon in Fig. S3a to S3h and argon gas in Fig. S3i to S3p, respectively.

The ionic state resolved photoelectron angular distributions

Figure S4a displays the PADs calculated using RMT for photoelectrons coupled to the P_0 -residual ionic state in neon at $\Theta_T = 0^\circ$, at a peak NIR intensity of $0.1\text{TW}/\text{cm}^2$. The one-photon ionization peaks display an angular character resulting from the interference of s - than d_0 -waves, where the yield of photoelectrons populated along $\theta = 0^\circ, 180^\circ$ is close to the yield of photoelectrons populated along $\theta = \pm 90^\circ$. At the sidebands, the photoelectron wave packet from two-photon ionization is the superposition of p_0 - and f_0 -waves, and tends to be polarized along $\theta = 0^\circ, 180^\circ$ (3). For residual ionic states with $P_{\pm 1}$ symmetry in Fig. S4b, the one-photon ionization peaks display a homogeneous four-fold structure since only $d_{\mp 1}$ -waves are populated by a single photon absorption in this case. The angular distribution of sideband

photoelectrons also shows a similar four-fold structure, arising from the interference of $p_{\mp 1}$ and $f_{\mp 1}$ -waves. Figure S4c is the incoherent sum of the PADs shown in Fig. S4a and S4b, the resulting one-photon ionization peaks display a more homogeneous distribution, and the dominant sideband yield is located along $\theta = 0^\circ, 180^\circ$. Figure S4d to S4f show the PADs for the same set of residual-ion states as shown in Fig. S4a to S4c, but for $\Theta_T = 90^\circ$. In this case, the sideband photoelectrons coupled to the P_0 -residual ionic state tend to be emitted along $\theta = \pm 90^\circ$ while those coupled to the $P_{\pm 1}$ -ionic states still show a four-fold structure. The total PADs of sideband electrons resulting from the incoherent sum of Fig. S4d and S4e are mainly emitted along $\theta = \pm 90^\circ$.

Figures S5 show the ionic state resolved PADs in argon, where the selected ionic states and the polarization of the NIR field are as the same as Figs. S4. Compared to neon, photoelectrons ionized by a single photon and coupled to the P_0 residual-ion state display an angular character similar to that of a d_0 -wave, which indicates that the one-photon induced population of the d_0 -state is more dominant in argon than in neon (4).

The ionic state resolved relative two-photon phase shift distributions

For neon and argon, with valence-shell p electrons, the degenerate P_0 and $P_{\pm 1}$ ionic states have perpendicular spatial polarization character, thus the incoherent ionization pathways are aroused. Our *ab initio* RMT calculation decomposed the sideband photoelectron wave-packet from two-photon transitions into residual ionic states and resolved the photoelectron partial waves. Since the ionic state remains constant during the two-photon transitions, the incoherent ionization pathways can thus be distinguished. Figure S6a displays the $\Delta\phi_{\text{rel}}^{\text{SB18}}$ of the photoelectrons coupled to P_0 residual ionic state at $\Theta_T = 0^\circ$ with a kinetic energy of 6.52eV. The purple lines with colors weighted by the relative photoelectron yields represents the RMT simulated results. According to the well-known dipole transition rules, the case of parallel XUV-APT and NIR fields only allows the interference of p_0 and f_0 -waves originating from the initial p_0 -state. The relative phase shifts show a four-fold θ dependence such that $\Delta\phi_{\text{rel}}^{\text{SB18}}$ displays a local maximum at the angle where the photoelectrons are most likely populated and gradually decreases to -0.52π as θ varies. Besides the *ab initio* simulation, we also provide an analytical expression based on partial wave interference in each ionic channel to reconstruct the angular character of $\Delta\phi_{\text{rel}}^{\text{SB}}$. In the simple model of partial wave interference in a single P_0 -ionic channel, the PADs,

$I_{P_0}^{SB18}$ and the relative emission angle resolved two-photon transition, $\phi_{P_0}^{SB18}$ can be described as:

$$I_{P_0}^{SB18}(\theta, \varphi, \Theta_T = 0^\circ) \sim \left| c_{10} Y_{10}(\theta, \varphi) e^{-i\phi_{p_0}^{2h\nu}} + c_{30} Y_{30}(\theta, \varphi) e^{-i\phi_{f_0}^{2h\nu}} \right|^2, \quad (2)$$

$$\phi_{P_0}^{SB18}(\theta, \varphi, \Theta_T = 0^\circ) \sim \arg \left[c_{10} Y_{10}(\theta, \varphi) e^{-i\phi_{p_0}^{2h\nu}} + c_{30} Y_{30}(\theta, \varphi) e^{-i\phi_{f_0}^{2h\nu}} \right] - \phi_{P_0}^{SB18}(\theta = 0^\circ, \varphi), \quad (3)$$

where the $|c_{lm}|^2$ and $\phi_{lm}^{2h\nu}$ are the amplitudes and two-photon transition phase shift of each partial wave. Here we employ the relative partial wave ratios and two-photon phase shifts extracted from the RMT simulation to reproduce the PADs and the angular distribution of $\Delta\phi_{\text{rel}}^{SB18}$. The results are shown by the red lines in Fig. S6a. The results of the partial wave interference model agree with the RMT simulation especially at the angles where most photoelectrons are emitted. Figure S6b displays the yield-weighted $\Delta\phi_{\text{rel}}^{SB18}$ of photoelectrons coupled to the P_0 ionic state at $\Theta_T = 90^\circ$. In this case, the partial wave interference gives a photoelectron yield $I_{P_0}^{SB18}$ is defined as:

$$I_{P_0}^{SB18}(\theta, \varphi, \Theta_T = 90^\circ) \sim |-ic_{11}[Y_{11}(\theta, \varphi) + Y_{1-1}(\theta, \varphi)]e^{-i\phi_{p\pm 1}^{2h\nu}} + ic_{31}[Y_{31}(\theta, \varphi) + Y_{3-1}(\theta, \varphi)]e^{-i\phi_{f\pm 1}^{2h\nu}}|^2. \quad (4)$$

As for the photoelectrons coupled to $P_{\pm 1}$, the initial $p_{\mp 1}$ states make transitions to $p_{\mp 1}$ and $f_{\mp 1}$ -waves in the case of parallel XUV-APT and NIR fields, whereas p_0 , f_0 and $f_{\pm 2}$ -waves may be populated at $\Theta_T = 90^\circ$. Thus the PADs for parallel and perpendicular relative polarization of the XUV-APT and NIR fields are described as:

$$I_{P_{\pm 1}}^{SB18}(\theta, \varphi, \Theta_T = 0^\circ) \sim \left| c_{1\mp 1} Y_{1\mp 1}(\theta, \varphi) e^{-i\phi_{p\mp 1}^{2h\nu}} + c_{3\mp 1} Y_{3\mp 1}(\theta, \varphi) e^{-i\phi_{f\mp 1}^{2h\nu}} \right|^2. \quad (5)$$

$$I_{P_{\pm 1}}^{SB18}(\theta, \varphi, \Theta_T = 90^\circ) \sim \left| -ic_{10} Y_{10}(\theta, \varphi) e^{-i\phi_{p_0}^{2h\nu}} + ic_{30} Y_{30}(\theta, \varphi) e^{-i\phi_{f_0}^{2h\nu}} + ic_{3\mp 2} Y_{3\mp 2}(\theta, \varphi) e^{-i\phi_{f\mp 2}^{2h\nu}} \right|^2. \quad (6)$$

As shown in the Fig. S6c and S6d, the $\Delta\phi_{\text{rel}}^{SB18}$ from the RMT simulation and partial wave interference model both display a four-fold angular structure. The inconsistencies between the two models may be attributed to the poor definition of the oscillation phase of photoelectrons close to the zeros of the PADs. The results for the NIR field polarized at an arbitrary angle can thus be taken as the superposition of the special cases of parallel and perpendicular relative polarization of the two fields, using Clebsch-Gordan coefficients. Figure S7 displays the ionic state resolved relative phase shift distributions, the $\Delta\phi_{\text{rel}}^{SB14}$ in argon which has similar angular character to the results in neon.

In order to uncover the initial distribution of P_0 and $P_{\pm 1}$ ionic states, we compare the summation of p_0, f_0 -waves with $p_{\mp 1}, f_{\mp 1}$ -waves at $\Theta_T = 0^\circ$ and the relative ratio is displayed in Fig. S8a. In general, photoelectrons coupled to the P_0 ionic state contribute more than those coupled to $P_{\pm 1}$, and the relative ratio increases slightly as a function of photoelectron kinetic energy. The result in argon has a larger value than neon, which indicates the ground state of valence electrons in argon populate more in p_0 -states. At $\Theta_T = 90^\circ$, we also show the relative ratio between the summation of $p_{\pm 1}, f_{\pm 1}$ -waves coupled to P_0 and p_0, f_0 and $f_{\pm 2}$ -waves coupled to $P_{\pm 1}$ in Fig. S8b, and the ratio, $R_{P_0/P_{\pm 1}}$ displays an opposite trend to that seen at $\Theta_T = 0^\circ$.

References and Notes

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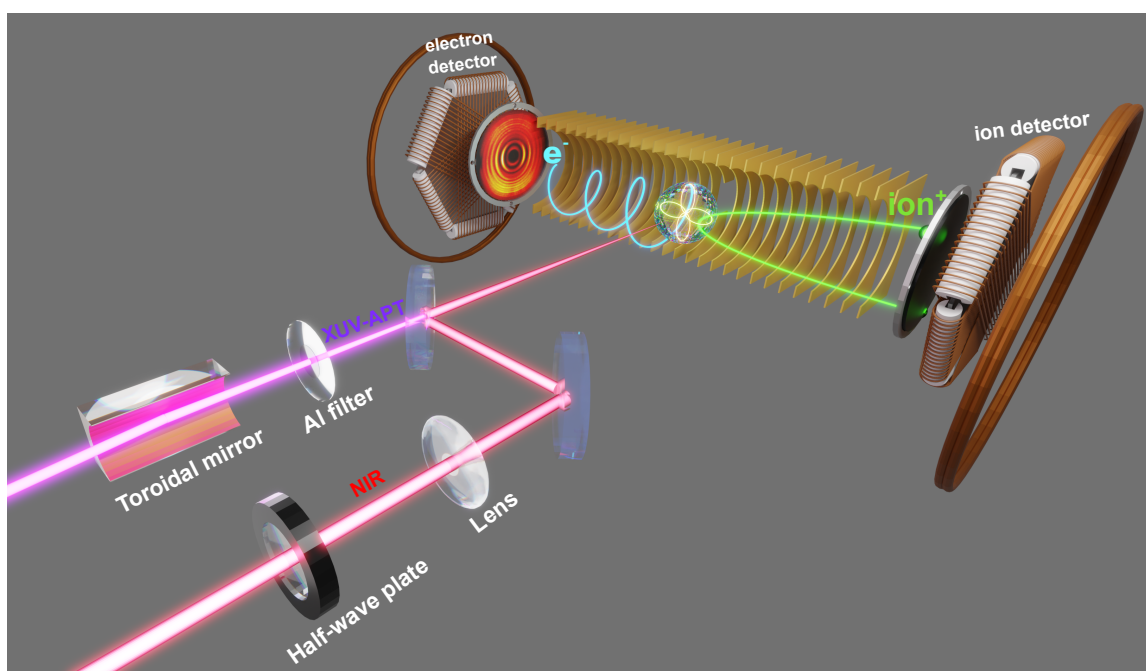


Fig.S 1: Schematic diagram of the cross-polarized attosecond interferometer. The XUV-APT is generated from dense Xe or Ar gas, and covers high harmonics combs from H11 to H15 or H13 to H25, respectively. The non-collinear XUV-APT and NIR field form a phase-locked Mach-Zehnder interferometer and are recombined via a holey mirror to perform RABBITT measurements in the reaction chamber of a Coltrims set-up.

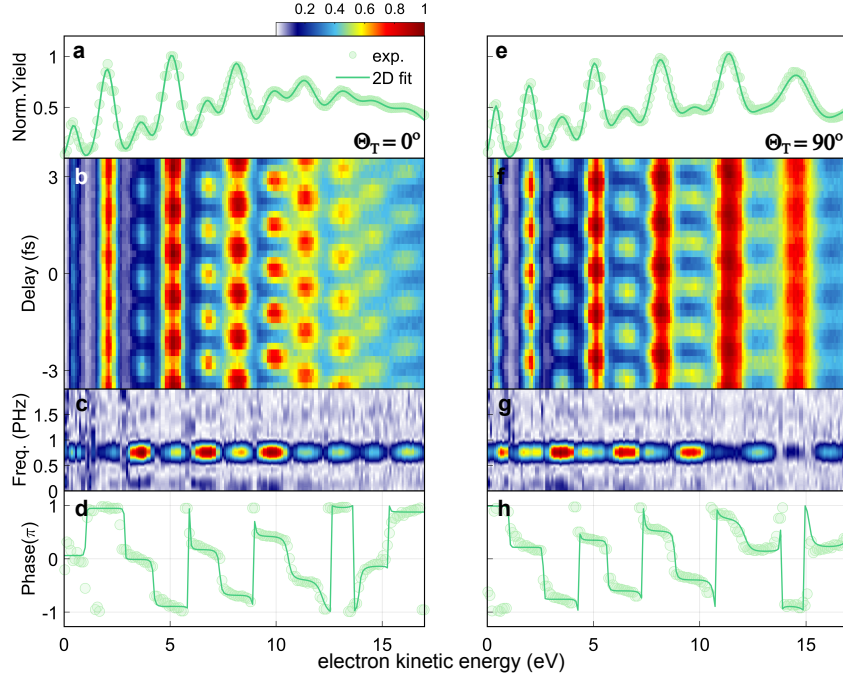


Fig.S 2: Geometry resolved sideband phase reconstruction in neon. **a.** The photoelectron kinetic energy spectrum at $\Theta_T = 0^\circ$. The green circles display the experimental measurements and the solid line is the fitted result determined from a multi-peak Gaussian fitting. **b.** The experimental RABBITT trace integrated over the photoelectron emission angle. **c.** The fast-Fourier amplitudes of oscillations with a central frequency of $2\omega_{\text{NIR}}$ as a function of the kinetic energy. **d.** The reconstructed two-photon phase shifts, ϕ_0 . The green circles are the direct fast-Fourier phase of the $2\omega_{\text{NIR}}$ oscillation and the solid line is the result from the reconstructed RABBITT spectrum via 2D-fitting. **e-f.** The sideband phase reconstruction process as in **a-d** but at $\Theta_T = 90^\circ$.

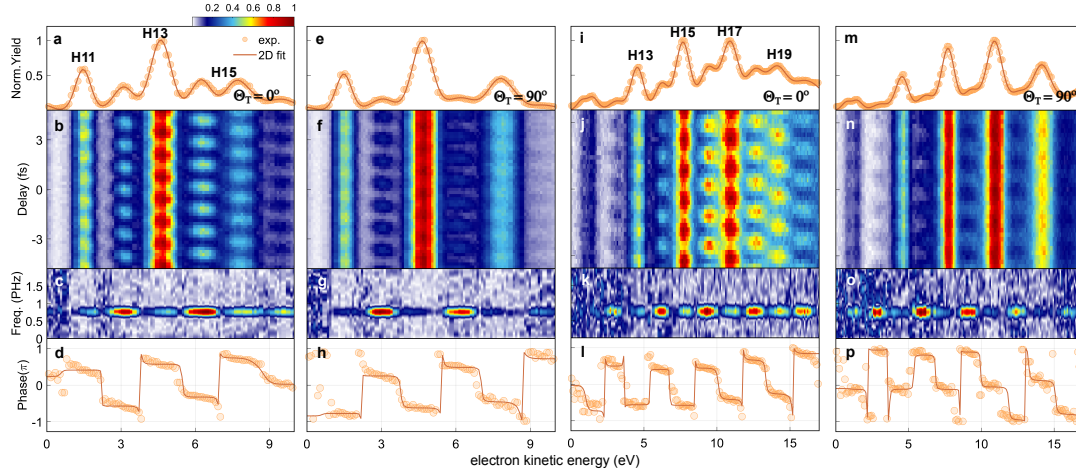


Fig.S 3: Geometry resolved sideband phase reconstruction in argon. **a-d.** The oscillation phase reconstruction in argon at $\Theta_T = 0^\circ$ as in Fig. S2a-S2d. The high harmonic combs generated from xenon gas covers from H11 to H15. **e-h.** The sideband phase reconstruction as in **a-d** for $\Theta_T = 90^\circ$. **i-p.** Same as **a-h** but the high harmonic combs generated from argon gas covers from H13 to H23.

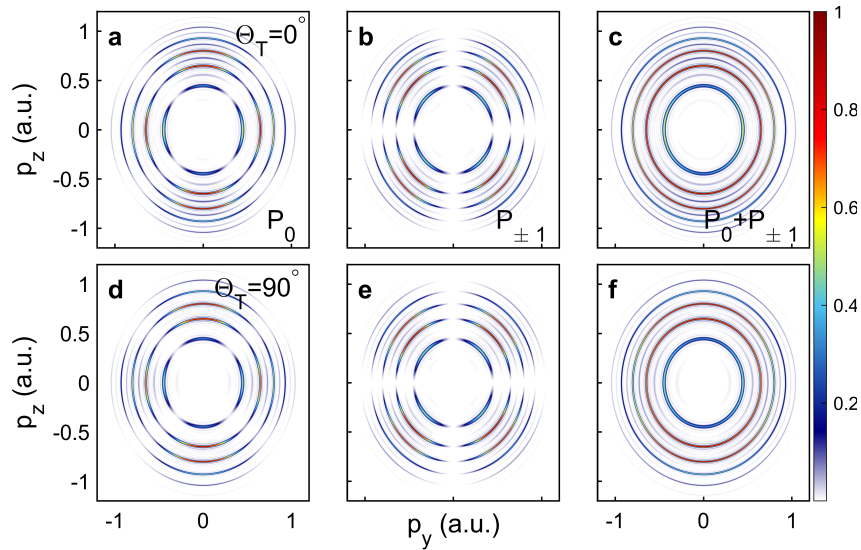


Fig.S 4: Residual ionic state resolved photoelectron angular distributions as a function of the skew angle in neon. **a-c.** The theoretical PADs of photoelectrons at $\Theta_T = 0^\circ$. The selected residual ionic state is **a** P_0 , **b** $P_{\pm 1}$ and **c** the incoherent sum of P_0 and $P_{\pm 1}$. **d-f.** The theoretical PADs of photoelectrons at $\Theta_T = 90^\circ$. The selected residual ionic states are the same as those in **a-c**. The simulated NIR peak intensity is 0.1 TW/cm^2 .

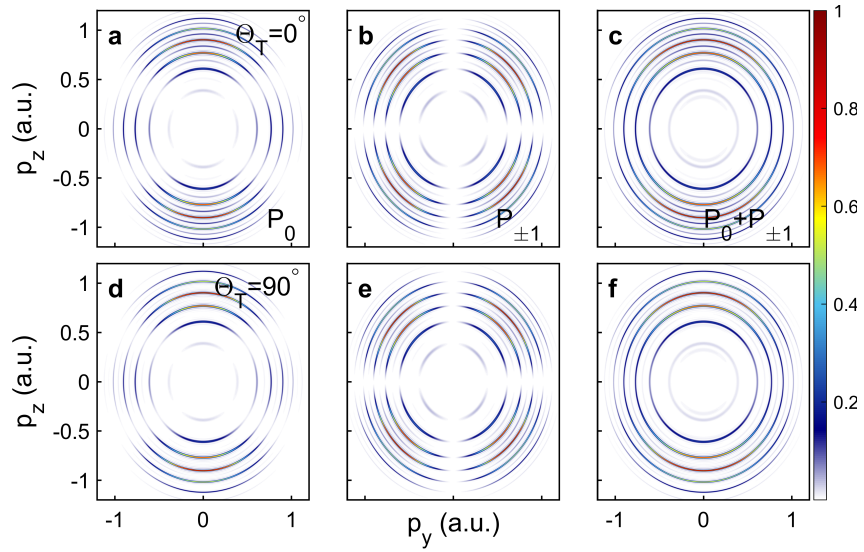


Fig.S 5: Residual ionic state resolved photoelectron angular distributions as a function of the skew angle in argon. **a-c.** The theoretical PADs of photoelectrons at $\Theta_T = 0^\circ$. The selected residual ionic state is **a** P_0 , **b** $P_{\pm 1}$ and **c** the incoherent sum of P_0 and $P_{\pm 1}$. **d-f.** The theoretical PADs of photoelectrons at $\Theta_T = 90^\circ$. The selected residual ionic states are the same as those in **a-c**.

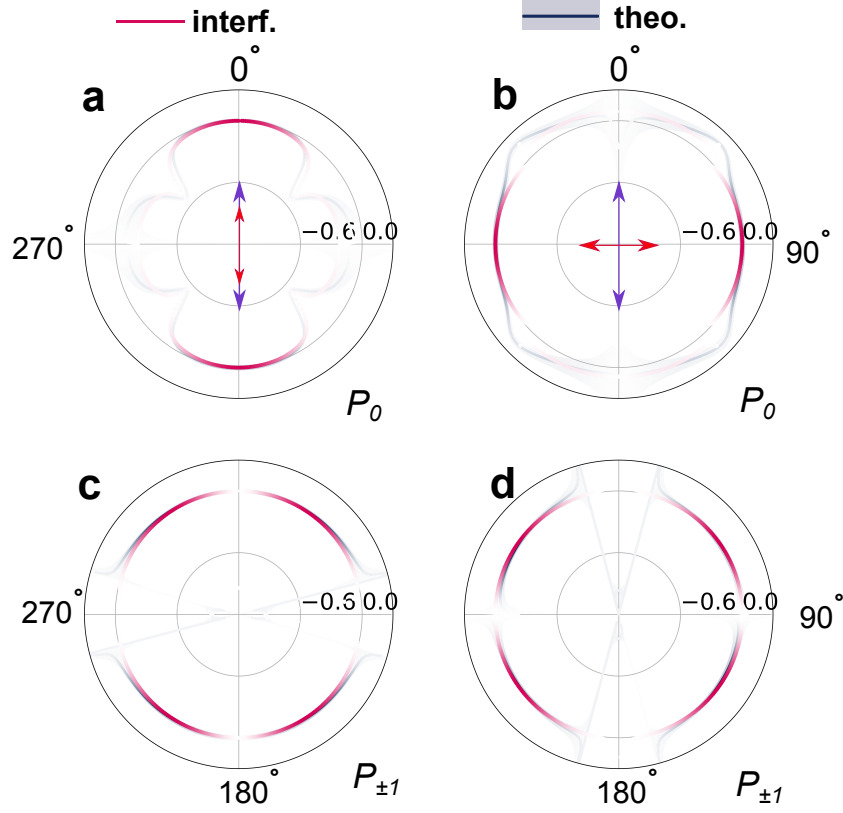


Fig.S 6: The ionic state resolved relative phase shift angular distributions of neon. a-b. The relative phase shift $\Delta\phi_{\text{rel}}^{\Theta_T}$ of photoelectrons coupled to the P_0 residual ionic state as a function of emission angle at $\Theta_T =$ **a** 0° , **b** 90° . The solid purple and red lines demonstrate the simulation from RMT and the direct results via partial wave interference including final p_0 , f_0 -waves in **a** and $p_{\pm 1}$, $f_{\pm 1}$ -waves in **b**. **c-d**. As in **a-b** but the photoelectrons are coupled to the $P_{\pm 1}$ residual ionic states.

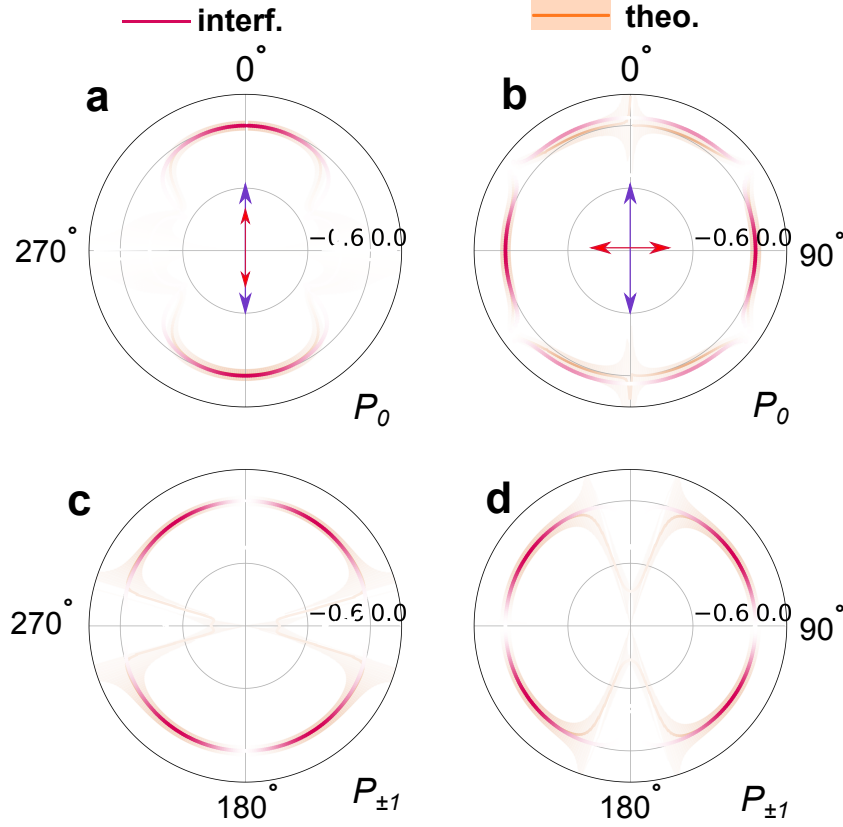


Fig.S 7: The ionic state resolved relative phase shift angular distributions of argon. The selected residual ionic state and the orientation state of the NIR field are the same as those in Fig. S 6.

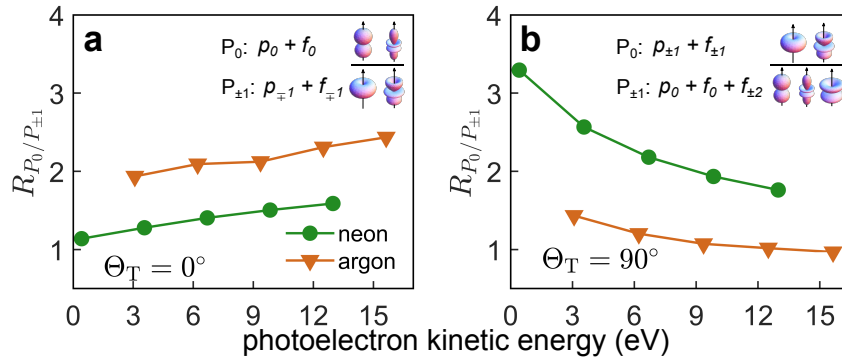


Fig.S 8: The calculated relative ratio of photoelectrons coupled to P_0 and $P_{\pm 1}$ ionic states. **a.** The ratio between p_0, f_0 -waves coupled to the P_0 -ionic state and $p_{\mp 1}, f_{\mp 1}$ -waves coupled to the $P_{\pm 1}$ -ionic state at $\Theta_T = 0^\circ$ as a function of photoelectron kinetic energy. Green and orange lines show the results for neon and argon, respectively. **b.** Relative ratio between the total yield of $p_{\pm 1}, f_{\pm 1}$ and $p_0, f_0, f_{\pm 2}$ at $\Theta_T = 90^\circ$.