

Spin-orbit and angle-resolved resonant attosecond photoionization delays

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Understanding how spin-orbit coupling shapes ultrafast electron dynamics remains a central challenge across atomic, molecular, and condensed-matter systems. Here, we demonstrate that spin-orbit splitting in krypton naturally separates two distinct regimes of attosecond interferometry: a conventional above-threshold process involving interference between continuum pathways and an under-threshold regime in which discrete and continuum intermediate states coexist and interfere. Using spin-orbit and angle-resolved measurements with attosecond precision, supported by *ab initio* time-dependent simulations, we reveal that the under-threshold channel exhibits dramatic phase and delay variations—up to several hundred attoseconds—highly sensitive to photon energy and emission direction. In contrast, the conventional above-threshold channel shows smooth, featureless behavior. This duality exposes the strong influence of metastable resonances, establishing spin-orbit splitting as a built-in control knob for accessing structured continua. Beyond krypton, our results provide a broadly applicable framework for probing and controlling coupled spin, orbital, and many-body correlation dynamics at the attosecond timescale.

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I. INTRODUCTION

Spin-orbit (SO) resolved electron dynamics has emerged as an important topic in attosecond science, offering direct insight into the interplay of relativistic effects, electron correlation, and coherence in ultrafast photoionization. Early studies established that photoemission delays differ not only between electronic shells but also between SO-split components of the same shell, as observed in krypton and xenon, with delays up to several tens of attoseconds [1]. These results underscored the central role of SO coupling in shaping attosecond dynamics, particularly in heavier atoms. Subsequent experiments refined this picture: Zhong *et al.* [2] demonstrated how the giant dipole resonance in xenon coexists with a narrow spin-flip resonance, whose interference drives SO-dependent emission delays, while Turconi *et al.* [3] disentangled overlapping SO components of autoionizing resonances in argon, resolving their decay dynamics on subfemtosecond timescales. Stewart *et al.* [4] extended these advances by directly imaging SO-driven hole dynamics in rare-gas cations, and Laurell *et al.* [5] introduced quantum-state tomography of photoelectrons, revealing how SO entanglement with the ionic core reduces state purity.

More recently, Alarcón *et al.* [6] observed quantum beats in two-color ionization of argon, where phase differences between SO-split continua reflected short-range electron-ion interactions.

In parallel, attosecond interferometric techniques, such as reconstruction of attosecond beating by interference of two-photon transitions (RABBITT), have been adapted to probe situations where one of the two-photon pathways proceeds through a bound intermediate state. This regime, known as under-threshold RABBITT (uRABBITT), turns the structure of discrete states—their energies, widths, and angular couplings—into directly measurable observables. Foundational work in helium established the feasibility of below-threshold interferometry, showing rapid phase variations as the excitation is tuned across discrete states [7]. Follow-up studies mapped phase jumps across resonances and antiresonances, demonstrating angular dependence from partial-wave interference [8] and clarifying the roles of resonant and antiresonant contributions [9]. More recently, momentum-resolved measurements reconstructed the anisotropy of the two-photon transition amplitude in helium [10], while resonance-assisted ionization in neon produced nearly pure higher- ℓ partial waves, yielding holographic images of the emission process [11]. Comparative studies of under- and above-threshold harmonics further showed how bound-state-mediated and nonresonant paths interfere [12], and heterodyne analyses revealed that even weak high-order partial waves can significantly reshape sideband (SB) anisotropy and phase [13]. In a recent publication, Li *et al.* [14] demonstrated partial wave interferometry between SO channels as the future of high-fidelity quantum measurements.

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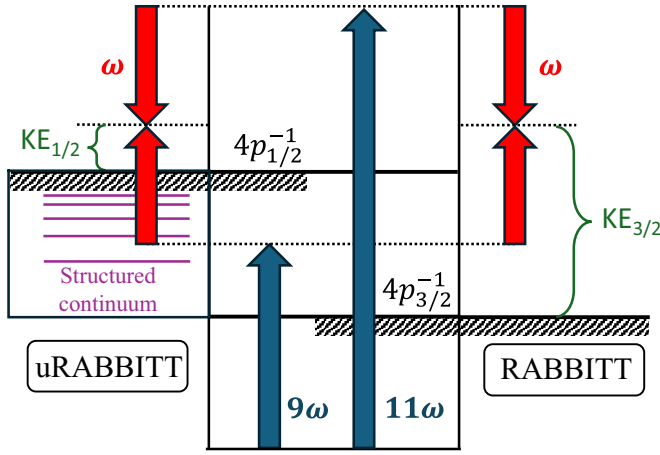


FIG. 1. Schematic for the RABBITT and uRABBITT in krypton, corresponding to $4p_{3/2}$ and $4p_{1/2}$ ionizations, respectively. Blue arrows represent odd harmonics and the red arrows denote single-photon transitions that generate interferences in the photoelectron kinetic energy (KE) spectra for both spin-orbit split channels. Interference in the uRABBITT process is strongly impacted by the presence of resonances between the two thresholds, leading to dramatic energy and angle dependence of attosecond photoionization delays.

In this work, we focus on the ionization from $4p$ shell of krypton, where both SO and uRABBITT themes converge to address an important question: How does the SO coupling reshape attosecond electron dynamics when discrete and continuum pathways coexist? At an appropriately chosen photon energy, ionization from the more weakly bound $4p_{3/2}$ state leads to conventional RABBITT involving two continuum pathways, while ionization from the more tightly bound $4p_{1/2}$ state gives rise to uRABBITT, where discrete and continuum intermediate states interfere (see Fig. 1). Access to the dual (RABBITT and uRABBITT) regime makes krypton an ideal platform to resolve the interplay of SO splitting and under-threshold interferometry. By combining precise angle-resolved measurements with *ab initio* simulations, we show how the conventional and under-threshold RABBITT regimes manifest themselves in distinct phase behaviors, thereby opening a route to directly probe the structure and dynamics of intermediate states in SO-split systems.

Previous investigations of resonant and under-threshold RABBITT dynamics in lighter atoms—helium [7–10], neon [11], and argon [12,15]—established the key principles of phase variation across discrete resonances and demonstrated the feasibility of probing bound-continuum interference with attosecond precision. However, these systems lack strong spin-orbit splitting and therefore do not permit a direct comparison between discrete-continuum and continuum-continuum pathways within a single atomic shell. In contrast, the $4p$ shell of krypton provides two naturally separated spin-orbit channels: the $4p_{3/2}$ state, which supports conventional RABBITT through interference of continuum pathways, and the more tightly bound $4p_{1/2}$ state, which enters the under-threshold regime where discrete and continuum intermediates coexist. This built-in dichotomy enables simultaneous observation of both interferometric mechanisms under identical

experimental conditions, offering a stringent benchmark for *ab initio* theory and revealing how spin-orbit coupling and near-threshold resonances jointly determine attosecond photoionization delays.

II. EXPERIMENTAL SETUP

The RABBITT experiments were performed in an actively stabilized attosecond pump-probe setup. We start with an ~ 40 fs 1.3 mJ near-infrared (NIR) pulse with a central wavelength of 780 nm and a repetition rate of 1 kHz from a commercial Ti:sapphire amplifier. The central wavelength can be tuned slightly by changing the dispersion compensation conditions in the Ti:sapphire oscillator. The central wavelength is characterized using a spectrometer with 0.5 nm resolution, which allows us to reliably measure 1 meV shift in the central photon energy. We have also investigated long-term variations of laser spectrum, and the central photon energy is stable below the instrumental resolution of 1 meV during the time delay scans. This pulse is split into two arms using a 50–50 beam splitter. One arm is focused into a 3.5-cm-long hollow-core waveguide to perform high harmonic generation (HHG) in xenon that produces an extreme ultraviolet attosecond pulse train (XUV-APT). A toroidal mirror is used in $2f$ – $2f$ imaging mode to focus the XUV-APT onto an effusive gas jet of krypton at the interaction region of a standard velocity map imaging (VMI) spectrometer.

The other arm of the pulse is used as a probe and delayed with respect to the XUV-APT using a piezo-stage and recombined with the XUV-APT colinearly using a custom mirror with two holes. A 1-m focal length lens is used in this arm right before the holey mirror to focus the beam at the same interaction point in the VMI spectrometer. The intensity of the NIR probe at the interaction point is estimated at approximately 10^{11} W/cm². The specially built pump-probe recombination mirror with two holes is also used to collect the residual driver from the XUV pump arm and the central part of the probe arm passing through the hole for active delay stabilization feedback loop. These two arms are overlapped on a separate CMOS camera to make our delay-stabilization interferometer (similar to Luo *et al.* [16]). By analyzing the interference fringe pattern on the camera, we use a real-time proportional feedback to actively stabilize the pump-probe time delay. Both the XUV-APT and the probe NIR are linearly polarized along the same direction. The polarization axis is chosen to be parallel to the plane of the photoelectron detector to ensure accurate Abel inversion.

In the current experiment, we use xenon as the HHG medium that provides significant improvement in photon flux in low-order harmonics. This is important for probing the under threshold dynamics of the system. Additionally, phase matching in the waveguide geometry [17] also allows for significant spectral tunability of the harmonics. This gives us immense flexibility in the current experiment where RABBITT phase is extremely sensitive to the photon frequency due to the presence of autoionizing Fano resonances in the system.

The VMI spectrometer used in our experiment is based on the basic three-electrode design of Eppink and Parker [18]. Photoelectron momentum images are recorded, centered, and symmetrized before performing numerical Abel inversion

(using pBASEX routine [19]) at each pump-probe time delay. Compared with other photoelectron spectroscopy techniques, velocity map imaging provides us with energy- and angle-resolved spectrograms. These spectrograms are integrated over emission angles to extract photoemission phases. Jordan *et al.* [1] have reported the angle-integrated SO photoemission time delays in conventional RABBITT regime. In this study, we extend these measurements to an under-threshold regime, where we see very distinct photon energy dependence of measured phases between SO channels. We have also measured the angle dependence of SO time delays in photoemission due to interference of different partial waves. To extract the angle-resolved phase information, we integrate the Abel inverted image only inside a small angular wedge. For our experiment, we have used 5° angular wedges.

The experimental schematic for our study is shown in Fig. 2(a) along with the delay-dependent differential photoelectron spectrogram. The SO-split valence ionization thresholds in krypton for $4p_{3/2}^{-1}$ and $4p_{1/2}^{-1}$ states are reported at energies of 14.00 and 14.66 eV, respectively [20]. The central photon energy of our 9th harmonic is around 14.31 eV, which is in between these two thresholds, whereas the other higher-order harmonics (11th and 13th) are above both the thresholds. In a conventional RABBITT scheme, ionization is driven by an XUV APT composed of odd harmonics (blue arrows) separated by 2ω , where ω denotes the fundamental photon frequency. When a weak, time-delayed NIR probe pulse is introduced, the absorption or emission of a single probe photon couples adjacent harmonic orders (red arrows). The resulting quantum interference between these two-photon pathways gives rise to quantum interference in the even-order sidebands of the photoelectron spectrum, whose phase encodes subcycle photoionization dynamics. In the uRABBITT regime, the lowest harmonic lies below the ionization threshold, and the absorption of one probe photon can lift an electron into the continuum at the sideband energy. The corresponding photoelectrons interfere with those generated directly by a higher harmonic, providing access to the RABBITT phase evolution across the ionization threshold. In krypton, the ninth harmonic contributes to the conventional RABBITT pathway for the $4p_{3/2}$ channel, while for the $4p_{1/2}$ channel, it participates in an uRABBITT process. Consequently, SB10 contains contributions from both above- and under-threshold pathways, leading to a pronounced photon energy and emission angle dependence of the RABBITT phases observed in both *ab initio* theory and experiment. By contrast, in SB12 both SO channels lie above threshold, enabling a direct comparison of angle and photon energy dependence of RABBITT phases between the uRABBITT and conventional RABBITT regimes. We associate the conventional and uRABBITT pathways with each SB in Fig. 2(b). By analyzing the RABBITT phases of the two lowest sidebands in krypton, we simultaneously obtain energy- and angle-resolved measurements across two SO channels and across two distinct RABBITT regimes, providing a convenient and reliable benchmark for further studies.

III. THEORY

We follow closely our previous works in which we investigated the uRABBITT process in He, Ne [21,22], and

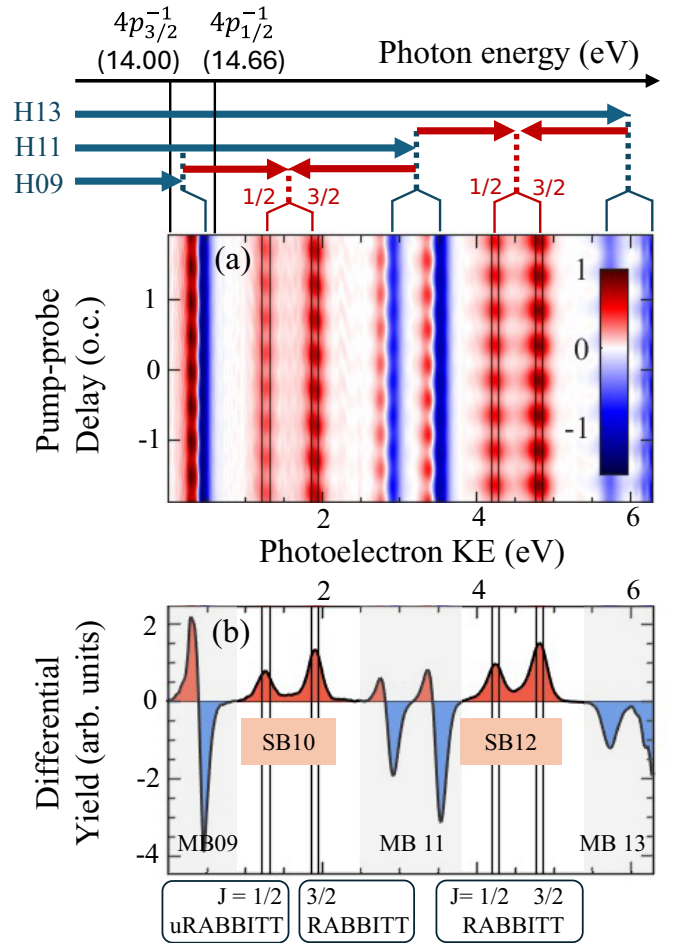


FIG. 2. (a) Time-delay-dependent differential, (XUV + IR) – (XUV), photoelectron spectrogram in Kr. Each responsible harmonic and sideband channel is shown with arrows on top. Odd-order harmonics (blue arrows) produce photoelectron main bands (MBs) and the single-photon transitions (red arrows) from the main bands produce even-order sidebands in photoelectron spectra, (b) The delay-integrated SO channels resolved differential spectrum showing the depletion (negative) of the main bands and the enhancement (red) of the side bands is shown against photoelectron kinetic energies. The vertical lines show the energy windows used for extracting RABBITT phase for each sideband.

Ar [15]. In brief, we solve numerically the time-dependent Schrödinger equation (TDSE) driven by a combination of an XUV-APT and an NIR pulse. Our TDSE solver is based on the spherical-coordinate implicit derivatives method [23]. The photoelectron momentum distribution (PMD) is obtained using the time-dependent surface flux method [24,25]. The target atom is described with a one-electron effective potential that is obtained by a local approximation to the Hartree-Fock method [26]. The validity of a single-electron effective potential model is systematically investigated for several noble-gas atoms in Ref. [27]. For heavier atoms such as krypton, the study shows that the single-active-electron approximation remains valid for photon energies below the $3d$ ionization threshold. In the present work, the photon energies used are well below the $3d$ threshold, and the dynamics probed are restricted to photoionization from the valence $4p$ orbital.

Under these conditions, multielectron correlation effects are expected to play a minor role, and the single-electron TDSE framework provides an adequate description of the dominant ionization pathways. The potential is cast into a split exponent form suggested by Muller [28]:

$$U(r) = Zr^{-1},$$

$$Z(r) = b \exp(-r) + (Z_0 - 1 - b) \exp(-ar) + 1. \quad (1)$$

Here, $Z(r)$ is the effective charge that tends asymptotically to the nuclear charge Z_0 when $r \rightarrow 0$. At the opposite limit, $Z(r) \rightarrow 1$ as $r \rightarrow \infty$. In the case of Kr, $Z_0 = 36$, $a = 5.50$, and $b = 9.30$ and 9.15 for the $4p_{1/2}$ and $4p_{3/2}$ initial states, respectively. With this choice, the bound state energies are $E_{4p_{1/2}} = -14.791$ eV and $E_{4p_{3/2}} = -14.148$ eV with the SO splitting $\Delta E = 0.643$ eV, which is close to the experimental value $\Delta E = 0.665$ eV [20]. The difference between the binding energies in theory and experiment is accounted for by a fine adjustment of the photon frequency.

In our numerical simulations, the XUV field represented by an APT is composed of 41 equally spaced pulselets of the opposite polarity:

$$A_x(t) = \sum_{n=-20}^{20} (-1)^n A_n \exp\left(-2 \ln 2 \frac{(t - nT/2)^2}{\tau_x^2}\right) \times \cos[\omega_x(t - nT/2)],$$

$$A_n = A_0 \exp\left(-2 \ln 2 \frac{(nT/2)^2}{\tau_T^2}\right). \quad (2)$$

Here, A_0 is the vector potential peak value, while $T = 2\pi/\omega$ is the period of the IR field.

The central XUV frequency ω_x and the time constants τ_x, τ_T are chosen to span a sufficient number of harmonics in the range of photon frequencies of interest. The IR pulse with the wavelength in the 800 nm range has a cosine squared envelope shifted from the center of the APT by a variable delay τ . The latter is incremented in seven steps by 10 a.u. = 240 as each. A wide IR pulse and the APT with a sufficiently large number of pulselets ensure the energy resolution in the photoelectron spectrum better than 0.2 eV. For the lowest SB10, this corresponds to sensitivity to the photon energy better than 0.02 eV.

In addition to this narrow-band XUV calculations, we conduct a wideband simulation with a single attosecond pulse (SAP) by restricting ourselves with the $n = 0$ term in Eq. (2). This way we can detect photoelectrons in a very broad energy range. The key element in such a calculation is to isolate the $2\omega\tau$ oscillation as in Eq. (3) from the much stronger $\omega\tau$ background. Numerical techniques used for removing this background are discussed in Refs. [29,30].

The PMDs returned by our TDSE simulation are integrated over the emission angle of the photoelectron to produce the angle-integrated photoelectron spectrograms. These spectrograms are shown in Fig. 3 for various photon frequencies and XUV/IR delay. The XUV-only contribution is subtracted from the spectra to eliminate much stronger primary harmonics for better clarity. The intensity calibration (in false colors) can be read from the sidebars in the rightmost panels. The SB orders are marked on all other panels. The top and bottom rows in

Fig. 3 correspond to the $4p_{1/2}$ and $4p_{3/2}$ initial states, respectively. The photon frequency varies from $\omega = 1.60, 1.57$, and 1.55 eV (from left to right). The SB centers are connected by the blue solid line to visualize the SB dispersion. This dispersion is provided by the RABBITT equation

$$S_{2q}(\tau) = A + B \cos(2\omega\tau - C), \quad C = \phi_{\text{at}} + \phi_{\text{XUV}}. \quad (3)$$

Here, A, B are the RABBITT magnitude parameters and C is its phase. The phase is composed of the atomic component ϕ_{at} and the instrumental contribution ϕ_{XUV} due to the APT chirp. The atomic phase $\phi_{\text{at}} = 2\omega\tau_a$ defines the atomic time delay $\tau_a = \tau_W + \tau_{\text{cc}}$, which is decomposed into the Wigner time delay τ_W and the continuum-continuum correction τ_{cc} [31].

We observe in Fig. 3 that for all the SBs their phase C is rather flat and changes very little with the order index $2q$. The only exception is the lowest SB10, whose center shifts very rapidly depending on the photon frequency ω . This shift, which is particularly strong for the tighter bound $4p_{1/2}$ initial state, manifests the onset of the uRABBITT regime. As the photon frequency varies, the primary harmonic peak H9, which is submerged below the ionization threshold, traverses the $4p^{-1}(^2P_{1/2}^0)nd$ Rydberg series. Accordingly, the interference between the discrete and continuous pathways goes through the series of peaks and troughs [30], which causes a very rapid variation of the uRABBITT phase.

This variation is highlighted in Fig. 4, where we plot the RABBITT phase parameter C entering Eq. (3) as a function of the photoelectron energy and the equivalent SB order $2q$. The photon frequency ω varies between 1.55 and 1.60 eV with a step of 0.01 eV. The top and bottom panels visualize the cases of $4p_{1/2}$ and $4p_{3/2}$ initial states. In the $J = 3/2$ case, the phase variation remains rather smooth reflecting the typical Coulomb behavior as it becomes stronger negative toward the threshold. In a very sharp contrast, the $J = 1/2$ case displays a very sharp phase variation in SB10, while all other SBs remain rather similar between the $4p_{1/2}$ and $4p_{3/2}$ initial states. Our experimental results in Sec. IV explore the contrasting behavior between SB10 and SB12, along with the dramatic dependence of SB10 phase on the IR frequency.

At large photoelectron energies $E \rightarrow \infty$, the RABBITT phase $C \rightarrow \phi_{\text{XUV}} = \pi$ in our simulations. This allows us to define the atomic time delay $\tau(E) = (C - \pi)/(2\omega)$, which is marked on the right vertical scale of Fig. 4. In the case of the $4p_{1/2}$ initial state, the time delay in SB10 varies by hundreds of attoseconds with a small change in the photon frequency ω . This is one of the distinct signs of the uRABBITT regime. The case of the $4p_{3/2}$ initial state is very different where the time delay varies very smoothly with the photoelectron energy E and the photon frequency ω , which is typical for a conventional RABBITT regime.

A similar observation can be made in Fig. 5, where we plot the RABBITT phase parameter C (in units of π) as a function of the photoelectron emission angle θ . The photon frequency $\omega = 1.567$ eV is chosen for the two cases of the $4p_{1/2}$ and $4p_{3/2}$ initial states (the top and bottom panels, respectively). These two cases are fairly similar in all respects except the SB10 behavior. In the case of the $4p_{1/2}$ initial state, SB10 splits from other SBs that are all close in the opposite $4p_{1/2}$ case.

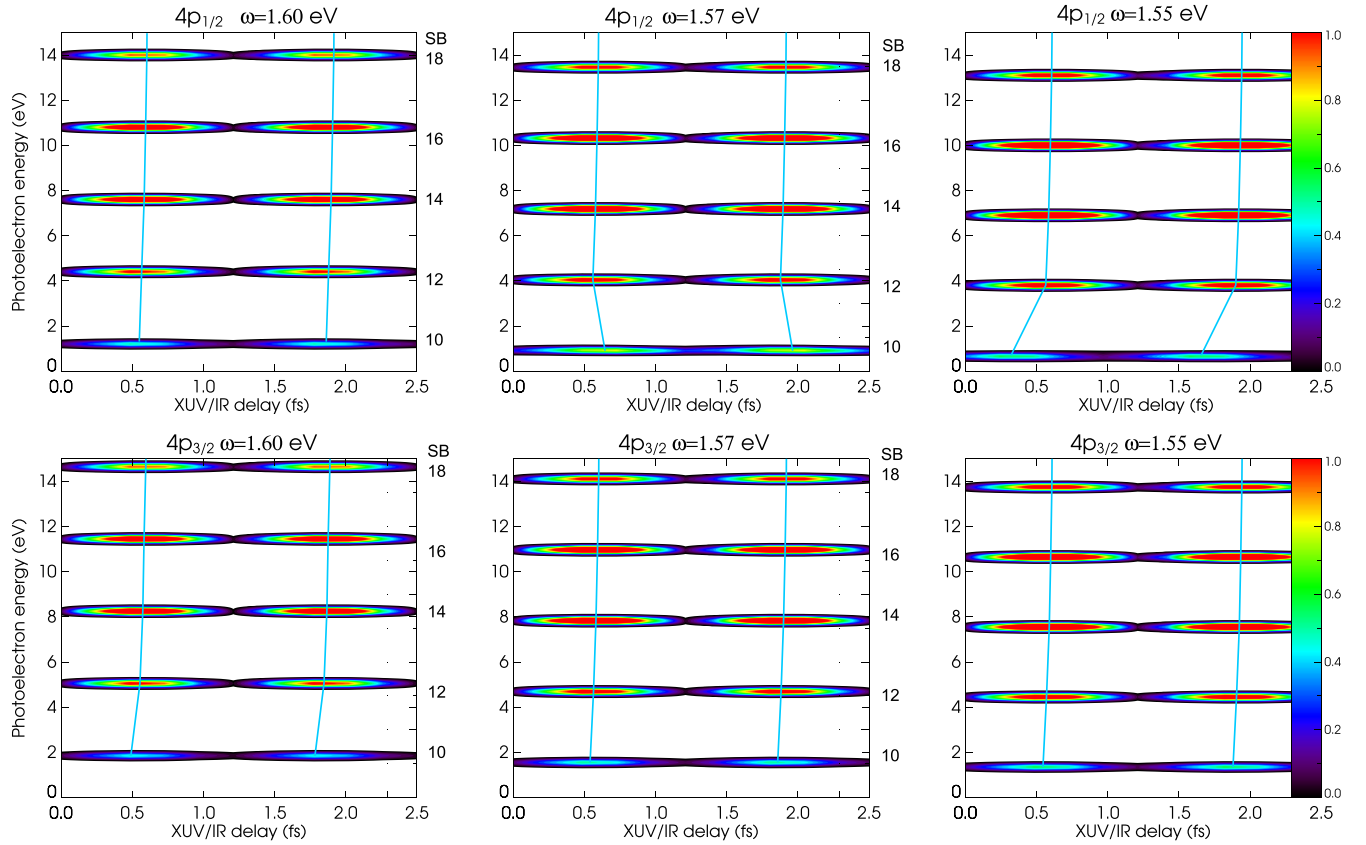


FIG. 3. Differential (XUV + IR) – XUV-only photoelectron spectra as functions of the energy (vertical scale, eV) and XUV/IR delay (horizontal scale, fs). The intensity calibration is shown on the color bars (rightmost panels). The SB order is marked on all other panels. The initial target states are $4p_{1/2}$ (top) and $4p_{3/2}$ (bottom). The laser frequency varies from $\omega = 1.60, 1.57$, and 1.55 eV (from left to right). The SB centers are connected by the blue solid line to guide the eye.

IV. EXPERIMENTAL RESULTS

A. Angle-integrated measurements

Time-delay-dependent angle-integrated differential photoelectron spectrogram for Kr $4p$ ionization is shown in Fig. 2(a). At each time delay, we record the XUV + NIR photoelectron spectrum and subtract the XUV-only spectrum to obtain the differential signal. The differential spectrogram has been normalized to a constant maximum followed by a frequency filtering that preserves the DC and the 2ω frequencies while filtering the high-frequency noise. The time delay between XUV-APT and NIR is shown in units of the optical cycle of the NIR pulse and we observe clear $2\omega\tau$ oscillations (3) with a period of half the optical cycle ($T = \pi/\omega$). In the differential spectrogram, red and blue correspond to the positive and negative signals, respectively. In the presence of the probe, main bands corresponding to the odd-order harmonics are depleted, and even-order sidebands appear in between them. Thus, in our differential spectrogram, the main bands appear in blue (negative), whereas the sidebands appear in red (positive). The delay-integrated differential spectrum is shown in Fig. 2(b), where the corresponding main bands and sidebands are marked with their SO splits. Energy windows of 100 meV width are used to extract lineouts for each of the sidebands. The vertical lines around the peaks of the sidebands are shown to mark the window for each sideband.

The differential photoelectron yields integrated over the energy window are shown in Figs. 6(a) and 6(b) for photon energies of 1.58 and 1.59 eV, respectively. For each photon energy, we look for the delay between the two SO channels for SB10 and SB12. The DC values [parameter A in Eq. (3)] have been subtracted in all cases. The fundamental photon energy is estimated from the central wavelength of the laser measured with a spectrometer. Each lineout has a sinusoidal $2\omega\tau$ RABBITT oscillation and the corresponding RABBITT phase is extracted from the fitting parameters [Eq. (3)]. The uncertainties in the measurement are estimated as 95% confidence intervals for each parameter. Now, looking back at Eq. (3), the oscillation phase for each sideband has a total contribution from the spectral phase difference between the neighboring harmonics (ϕ_{XUV}) and the atomic phase (ϕ_{at}) emerging from the complex two-photon matrix elements for photoionization that is specific to the system under study. By comparing the relative phases between the different SO thresholds for the same sideband, we can cancel the attochirp contribution (ϕ_{XUV}) and extract the two-photon atomic delays between the SO channels. We repeat this measurement by slightly tuning the central wavelength of the laser to look for photon energy dependence of SO time delays.

The two rows in Fig. 6(a) correspond to the SB10 and SB12 yields, respectively, for fundamental photon energies of 1.58 eV. The solid lines in each case show the best sinusoidal

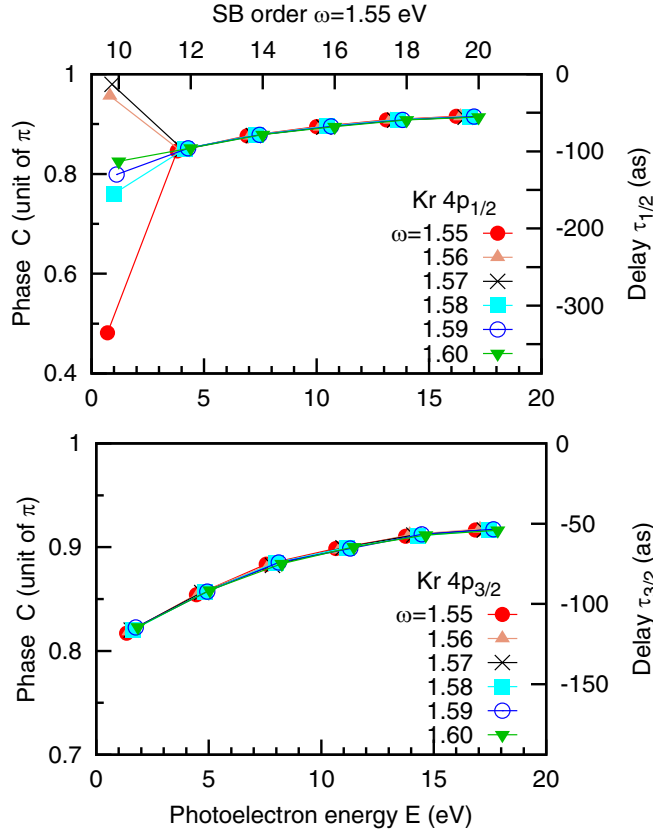


FIG. 4. RABBIT phase parameter C (in units of π) as a function of the photoelectron energy E (in eV) is shown for various photon frequencies ω . The top and bottom panels visualize the cases of the $4p_{1/2}$ and $4p_{3/2}$ initial states, respectively. The SB order $2q$ corresponding to $\omega = 1.55$ eV is marked on the top panel. The time delay $\tau = (C - \pi)/(2\omega)$ is marked on the right vertical axis.

fits for the $J = 3/2$ (blue) and $J = 1/2$ (orange) channels. We clearly observe a large 207 as delay between $J = 3/2$ and $J = 1/2$ photoionization channels for SB10, whereas we measure only a 14 as time delay between the channels in SB12. In Fig. 6(b), the same measurements are shown for a photon energy of 1.59 eV. The corresponding time delays measured in this case between the two SO channels are -66 and 2 as for SB10 and SB12, respectively. The two-photon time delays between the $J = 3/2$ and $J = 1/2$ channels are calculated from C parameters as $(C_{3/2} - C_{1/2})/2\omega$. The measured delay values are listed in Table I.

The angle-integrated measurements reveal two particularly striking features. The first is the presence of very large time delays—exceeding ~ 200 as—between the SO channels in SB10, in sharp contrast to the much smaller delays of order

TABLE I. Measured photoionization time delay between SO channels for two sidebands integrated over emission angle.

Sidebands	$\tau_{3/2} - \tau_{1/2}$ (as)	
	$\omega = 1.58$ eV	$\omega = 1.59$ eV
SB10	207.2 ± 14.8	-66.0 ± 7.8
SB12	14.0 ± 16.4	2.3 ± 7.0

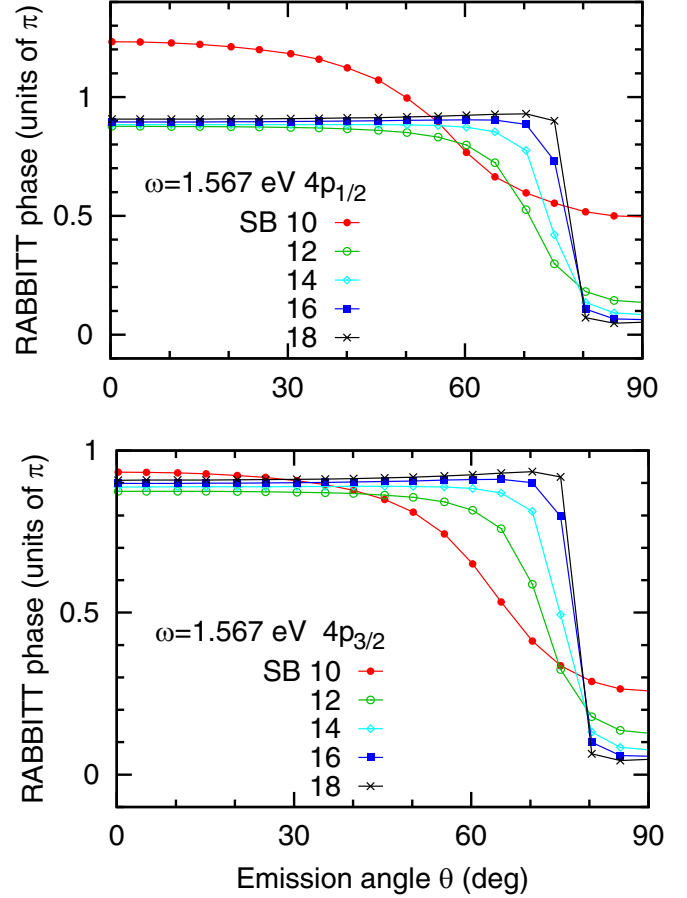


FIG. 5. RABBIT phase parameter C (in units of π) as a function of the photoelectron emission angle θ (in degrees) is shown for various SB orders $2q$. The photon frequency $\omega = 1.567$ eV. The top and bottom panels visualize the cases of the $4p_{1/2}$ and $4p_{3/2}$ initial states, respectively.

~ 10 as observed in SB12. This pronounced difference directly reflects the role of the under-threshold contribution in the $J = 1/2$ channel of SB10, whereas in SB12 both channels participate only through conventional RABBIT pathways involving continuum-continuum transitions.

The second observation concerns the extreme sensitivity of the SB delays to the central photon energy. A change of only ~ 10 meV in the driving photon energy is sufficient not only to significantly alter the magnitude of the delays but also to induce a reversal of their relative sign between the two SO channels. Such sensitivity is remarkable given that SB12 exhibits no measurable variation within the same photon energy window, remaining robust against small spectral shifts within our experimental uncertainties. These contrasting behaviors emphasize that the under-threshold component in SB10 amplifies the influence of spectral tuning, thereby rendering the time delays highly dispersive with respect to photon energy.

These effects are summarized in Fig. 7, where the experimentally measured SO RABBIT delays are shown alongside the corresponding two-photon delays obtained from *ab initio* simulations. The level of agreement between experiment and theory is striking, with only an offset of ~ 30 meV in the IR photon energy values. This discrepancy can be traced

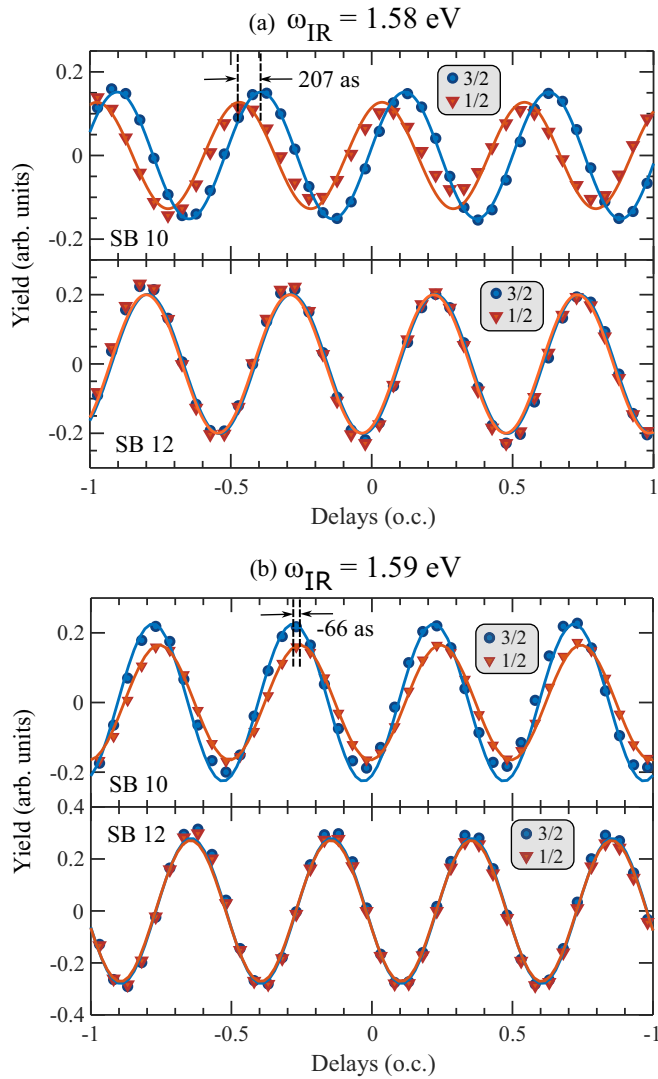


FIG. 6. (a) Angle-integrated photoelectron yield (DC subtracted) as a function of time delay for fundamental photon energy of 1.58 eV. Experimental data points are shown with markers and the corresponding sinusoidal fits are shown with solid lines. Sidebands 10 and 12 are shown in top and bottom rows for comparisons. For each sideband, we have two SO thresholds, dark blue corresponds to the $J = 3/2$ threshold and orange corresponds to the $J = 1/2$ threshold. (b) Same as panel (a) but for fundamental photon energy of 1.59 eV.

primarily to two factors: (1) The SO splitting obtained from the TDSE simulations with a one-electron model potential, 0.643 eV, is slightly underestimated compared to the experimental value of 0.665 eV and (2) the frequency bandwidths used in experiment and simulation differ. In particular, the numerical simulations presented in Fig. 7 employ a significantly longer attosecond pulse train, and thus a narrower bandwidth, to more clearly resolve the photon energy sensitivity of the phase.

Despite these differences, the agreement extends not only to the absolute delays but also to the observed energy dependence, confirming that the essential physics is well captured by the theoretical model. The pronounced sensitivity of SB10 to small spectral shifts—absent in SB12—establishes under-

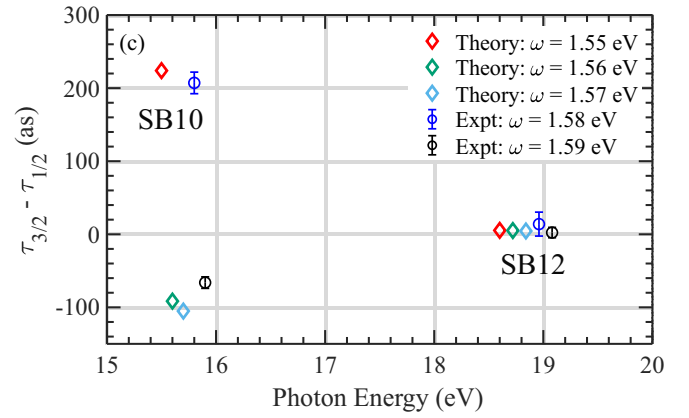


FIG. 7. Experimentally measured two-photon photoionization time delays between $J = 3/2$ and $J = 1/2$ channels are shown for two different IR photon energies ($\omega = 1.58$ and 1.59 eV). The experimental delays are compared alongside the theoretical values obtained from *ab initio* simulations for $\omega = 1.55$, 1.56, and 1.57 eV. The x axis corresponds to the two-photon energy calculated as the product of the sideband order and the fundamental photon energy ω .

threshold RABBITT as a powerful probe of the structured continuum between the SO thresholds where intermediate resonances play a central role. The physical origin of this enhanced sensitivity is further elucidated in the following section through broadband XUV-SAP simulations, which provide additional insight into the microscopic mechanisms driving the observed delays.

B. Angle-resolved measurements

In addition to angular integrated results presented in Sec. IV A, we also measured the SO time delays $\Delta\tau_{3/2-1/2}$ as a function of the photoelectron emission angle using the full momentum imaging capability of a VMI spectrometer. The delay between $J = 3/2$ and $J = 1/2$ channels measured at the photon energy $\omega = 1.59$ eV is shown in Fig. 8. The abscissa of Fig. 8 corresponds to the photoelectron emission angle measured with respect to the electric field polarization direction. Comparison with theoretical predictions shows the best agreement at $\omega = 1.567$ eV. A slight adjustment of the photon energy is in line with our angle-integrated measurements.

In our measurements, SB10 and SB12 exhibit markedly different angular characteristics in the SO time delay, underscoring the unique role of the uRABBITT contribution to the dynamics. This distinction highlights the sensitivity of the process to the relative positioning of the harmonic energies with respect to the SO thresholds. A more detailed understanding of this behavior is developed in the following section through *ab initio* simulations using a wideband XUV SAP, which provides valuable theoretical context for interpreting the experimental observations.

Another important feature is the pronounced dependence of the time delay on the photoelectron emission angle. While conventional angle-integrated measurements yield a single effective time delay value (shown in black dashed lines in Fig. 8), such integration inherently obscures the rich angular

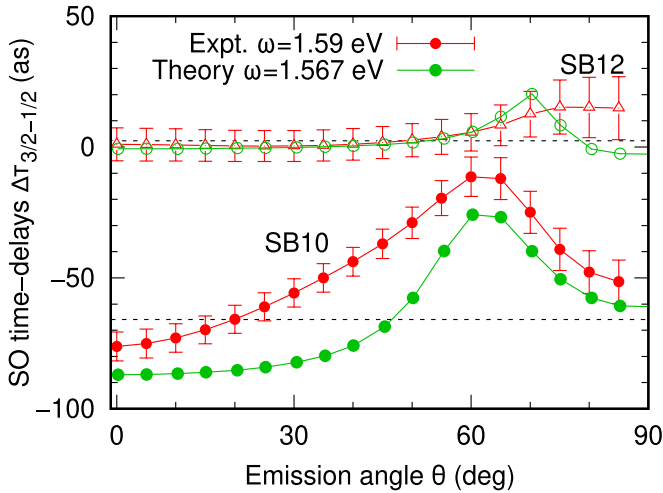


FIG. 8. Two-photon photoionization time-delay differences $\Delta\tau_{3/2-1/2}$ in Kr as a function of the photoelectron emission angles. The angles are measured with respect to the light polarization direction. Measurements taken at $\omega = 1.59$ eV are best matched with the calculation performed at $\omega = 1.567$ eV. Black dashed lines correspond to experimentally measured angle-integrated time delays from Table I for reference.

structure present in the data, especially for the uRABBITT regime. In contrast, the angle-resolved analysis reveals significant variations in the RABBITT phase as a function of emission direction. This anisotropy directly reflects the underlying interference between multiple partial-wave channels and thus serves as a sensitive and differential probe of photoemission dynamics in the system. In this way, angle-resolved RABBITT measurements provide a far more nuanced picture of electron dynamics than their angle-integrated counterparts, opening a window onto the interplay between SO coupling, continuum-continuum transitions, and many-body correlation effects.

V. DISCUSSION: THEORY VERSUS EXPERIMENT

In this section, we bring together our experimental findings and *ab initio* simulations to develop a coherent picture of the observed dynamics. One of the most striking experimental results is the sharp change in the sign of the SO time delay between the $J = 3/2$ and $J = 1/2$ channels in SB10 with a slight shift of the IR frequency as shown in Figs. 6(a) and 6(b). The TDSE simulations using a narrow-band XUV APT (Fig. 4) reproduce this behavior remarkably well, showing a strong phase variation in the $4p_{1/2}$ channel, while the $4p_{3/2}$ phase remains comparatively flat. When the experimental data are compared directly with the theory (Fig. 7), the two are found to be in close quantitative agreement once a small fundamental photon energy shift of about 30 meV is applied as discussed in Sec. IV A.

This excellent agreement confirms that the underlying physical mechanism is captured by the simulations, but it also raises an important question: What drives such a rapid phase variation in the under-threshold region? We attribute this behavior to the ninth harmonic's passage through a manifold of discrete $4p^{-1}(^2P_{1/2}^0)nd$ resonances in krypton. These

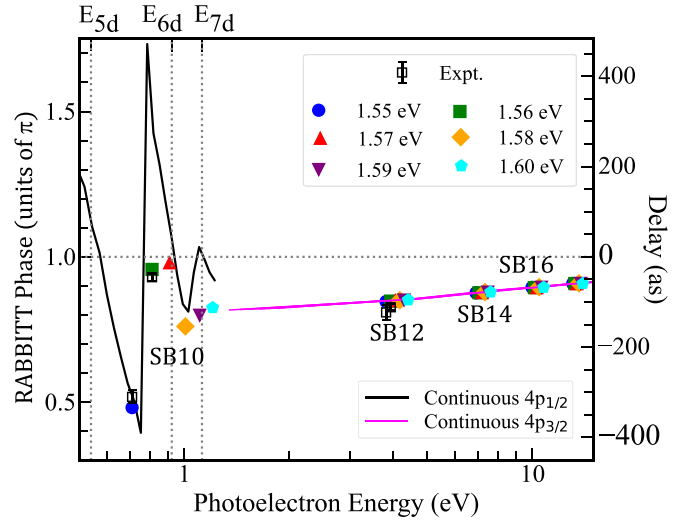


FIG. 9. RABBITT phase parameter C (in units of π) as a function of the photoelectron energy E (in eV). The wideband calculations are visualized with continuous solid lines for $4p_{1/2}$ (black) and $4p_{3/2}$ (magenta). The narrow-band $4p_{1/2}$ calculations with various photon frequencies ω are displayed with data points. The corresponding time delay $\tau = (C - \pi)/(2\omega)$ is marked on the right vertical axis. The photoelectron energies corresponding to the IR ionization of discrete $4p^{-1}nd$ excitations are marked on the top horizontal axis. The experimental SO delays tabulated in Table I are converted to the $4p_{1/2}$ delay by referencing to the flat $4p_{3/2}$ phase in the wideband simulation.

resonances form a “structured continuum” near threshold, where discrete Rydberg states form intermediate step in the two-photon transition to the continuum. As the harmonic energy moves across this region, the phase of the outgoing photoelectron wave packet becomes strongly dispersive and oscillates rapidly across the resonances. The precise locations and strengths of these resonances are highly sensitive to the details of the single-electron model potential used in the TDSE simulations, which may differ slightly from the true atomic potential. This sensitivity explains why a small adjustment of the photon energy is needed to align theory and experiment. Nonetheless, the qualitative features—most notably, the strong photon-energy-dependent phase modulations—are consistently reproduced, affirming that the observed effect originates from this interplay between the ninth harmonic spectrum and the structured continuum. To explore this mechanism in greater depth, we extended our analysis to an extra set of simulations using a broadband XUV SAP. Unlike the discrete harmonic case, the SAP excitation provides a continuous spectral window across the threshold, allowing us to map the evolution of the photoelectron phase without being constrained to specific sidebands.

All these results—namely, the experimental measurements, the narrow-band XUV APT simulations, and the broadband XUV SAP simulations—are presented together in Fig. 9. This figure provides a unified view in which theory and experiment converge, offering a comprehensive picture of the underlying dynamics in both the uRABBITT and conventional RABBITT regimes. The comparison reveals how the phase landscape evolves across the resonance series for

the uRABBITT regime. The individual components of this figure are discussed in detail below.

The solid black and magenta lines in Fig. 9 represent the results of the broadband XUV SAP simulations, showing the continuous variation of the RABBITT phase (in units of π) for the $4p_{1/2}$ and $4p_{3/2}$ ionization channels, respectively. Consistent with our previous narrow-band simulations, we set $\phi_{\text{XUV}} = \pi$, corresponding to zero time delay (indicated by the dashed horizontal line), and RABBITT phases for both $J = 3/2$ and $J = 1/2$ channels are separately measured relative to this reference. The horizontal axis denotes the expected photoelectron energy associated with the two-photon ionization to the two SO-split ionic thresholds.

Photoelectron energies below 0.5 eV are omitted, as they fall outside the range relevant to the present experiment. The $4p_{3/2}$ channel begins near 1.1 eV—approximately 0.6 eV higher than the $4p_{1/2}$ channel—consistent with the SO splitting in krypton. Notably, the $4p_{1/2}$ phase exhibits a series of pronounced oscillations as the XUV spectrum traverses the $4p^{-1}(^2P_{1/2}^0)nd$ excitation series, whereas the $4p_{3/2}$ phase remains relatively smooth. The positions of these resonances (ε_{nd}) are projected onto the photoelectron energy axis using $E_{nd} = \varepsilon_{nd} + \omega - IP_{1/2}$, where ω is the NIR photon energy and $IP_{1/2}$ is the ionization potential for the $J = 1/2$ channel obtained from the TDSE simulations. Sharp phase jumps and sign reversals are observed across the resonance positions, explained by the nodal structure of the two-photon ionization amplitudes [30]. The magnitude of this oscillation, initially close to π , gradually decreases toward the threshold as the spacing between discrete excitations becomes smaller than the spectral width of the IR pulse.

To verify consistency between the narrow-band and broadband XUV simulations, the discrete RABBITT phases from Fig. 4 are also included in the same figure. In this case, the photon energies corresponding to the sidebands are mapped onto the photoelectron energies. The data points from the SAP and APT simulations exhibit broadly consistent trends, as expected.

The final components of Fig. 9 are the experimental data points, shown as black markers with associated error bars. A general limitation in any experimental RABBITT measurement is that the measured phases are referenced to the attochirp-related XUV phase difference between the neighboring harmonics, ϕ_{XUV} . To position the experimental data points in Fig. 9, the measured delay differences between the $J = 3/2$ and $J = 1/2$ channels are first converted into the absolute $4p_{1/2}$ phase using the broadband SAP simulation $4p_{3/2}$ channel phase as a reference. The $4p_{3/2}$ phase (solid magenta line in Fig. 9) remains flat near SB10, as this channel does not go through any intermediate resonances. This constant phase background allows us to convert the relative delay differences (Table I) into absolute $4p_{1/2}$ delays and the corresponding phase values. These phases are then shifted by the theoretical reference phase $\phi_{\text{XUV}} = \pi$, which defines the zero-delay condition throughout our calculations. Finally, the experimentally measured fundamental photon energies are reduced by 30 meV before converting them to the photoelectron energy scale of Fig. 9, ensuring consistency with the photon energy offset identified between theory and experiment in the previous section. With these adjust-

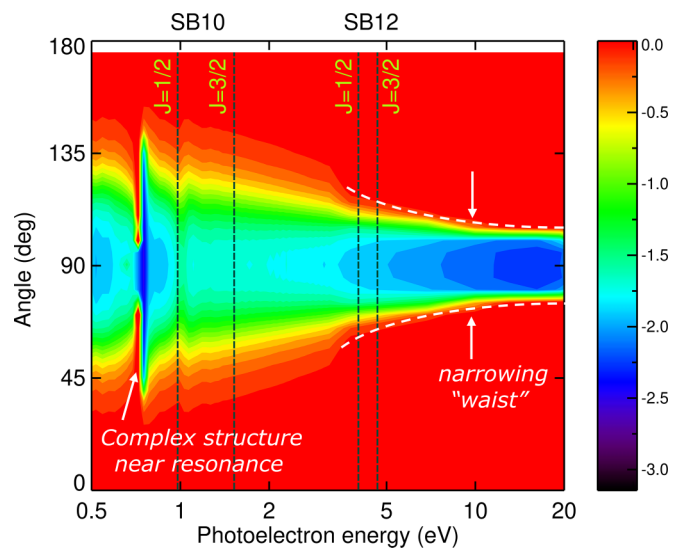


FIG. 10. Angular variation of the RABBITT phase $C(\theta) - C(\theta = 0)$ across a continuous range of photoelectron energies. The phase is encoded in false colors, ranging from 0 (red) to $-\pi$ (blue). Vertical lines mark the photoelectron energies in SB10 and SB12 with the $J = 1/2$ and $J = 3/2$ ionization thresholds.

ments, the experimental data points agree well with theoretical predictions.

The same wideband XUV SAP simulations are used to interpret and to reconcile the angular resolved RABBITT phases obtained in theory and experiment. The continuous mapping of the angular variation of the RABBITT phase relative to the zero-angle photoelectron emission direction is displayed in Fig. 10. This mapping is shown on the logarithmic photoelectron energy scale to highlight the most important low-energy range overlapping with discrete excitation energies E_{nd} . The vertical scale marks the emission angle θ counted from the polarization direction $\theta = 0$. The whole 180° angular range is covered for better clarity. The color bar indicates the phase variation $C(\theta) - C(\theta = 0)$, ranging from 0 (red) to $-\pi$ (blue).

Figure 10 displays the three distinct behaviors of the angle-resolved phase. At higher photoelectron energies well above the discrete excitations, the angular dependence of the phase changes gradually. The dip of the phase near $\theta = 90^\circ$ becomes deeper and tends to $-\pi$, while the “waist” around this dip becomes progressively narrower. This way the angular dependence tends gradually toward the stepfunction. Such a behavior can be seen in Fig. 5. It is well documented [27,32–34] and can be explained by the gradual convergence of the two-photon ionization amplitudes in the IR absorption and emission channels. In the meantime, when the photoelectron energy decreases, the two-photon ionization amplitude becomes disparate. The Fano’s propensity rules favor absorption of the IR photon when the photoelectron angular momentum is increased in result of this absorption [35]. Conversely, it is the emission of the IR photon that becomes favored. Such a disparity between the absorption and emission channels leads to the widening and flattening of the angular dependent phase as can be clearly seen in Fig. 10. Finally, near the discrete excitation energies E_{nd} , the ionization amplitudes in

the absorption channel become very oscillatory to the point of breaking the Fano's propensity rule [30]. Accordingly, the angular variation of the phase changes rapidly even with a small change of the photoelectron energy. Periodically, it can acquire a narrow waist that is more typical for the higher photoelectron energies.

These observations allow us to interpret the experimental and theoretical results shown in Fig. 8. For SB12, different ionization thresholds in the $J = 1/2$ and $J = 3/2$ ionization channels and the corresponding shift in the photoelectron energy change the angular dependent phase insignificantly. With larger photoelectron energy in the $J = 3/2$ channel, the "waist" is narrowing and the dip is getting deeper. So, the phase difference $\Delta\phi_{3/2-1/2}$ is first increasing slightly and then decreasing toward the emission angle $\theta = 90^\circ$. The angular variation of the phase difference is very different for the uRABBIT SB10. Here, the angular dependence of the $J = 1/2$ phase changes very rapidly and the area of a larger "red" phase extends into the regions of smaller yellow and green phase values. Hence, the difference $\Delta\phi_{3/2-1/2}$ becomes large and negative reaching the maximum magnitude close to the "magic" angle of 57° .

VI. CONCLUSIONS AND OUTLOOK

We have performed angle- and spin-orbit-resolved RABBITT measurements in the valence $4p$ shell of krypton, supported by *ab initio* time-dependent simulations. The spin-orbit partners naturally separate into two distinct interferometric regimes: conventional RABBITT, involving interference of two continuum pathways, and under-threshold RABBITT (uRABBITT), where discrete and continuum states interfere. This duality manifests most clearly in sideband 10, where the $J = 1/2$ channel exhibits large, photon-energy-dependent phase shifts reaching several hundred attoseconds, while the $J = 3/2$ channel shows smooth behavior characteristic of conventional RABBITT.

Our angle-resolved analysis further revealed pronounced anisotropies in the extracted delays, consistent with partial-wave interference, and reproduced by detailed numerical simulations. More broadly, these findings demonstrate that angle-resolved RABBITT is capable of probing electron dynamics in a regime where spin-orbit coupling, correlation, and continuum-continuum interactions all contribute on a comparable footing. This expands the scope of attosecond interferometry beyond the effective one-dimensional picture often assumed in angle-integrated approaches. Similar effects have been hinted at in other systems where threshold proximity or channel competition plays a role, but krypton provides a particularly clear benchmark case where both above- and under-threshold pathways from a single atomic shell can be directly contrasted within the same measurement. By capturing these subtleties, angle-resolved RABBITT opens the door to studying correlation-driven phase shifts, multichannel interference, and the angular fingerprints of spin-orbit dynamics with unprecedented detail.

Beyond krypton, the present approach illustrates how spin-orbit splitting can be leveraged to open complementary

interferometric channels, providing direct access to intermediate-state structure and dynamics. This capability is broadly relevant for studies of heavier atoms where relativistic effects are stronger, as well as in molecules and condensed matter, where discrete-continuum state interplay often governs the ultrafast photoionization. In this way, our work establishes a general strategy for using spin-orbit splitting as a built-in control knob to access both resonant and nonresonant two-photon pathways. Future extensions could exploit polarization control, different photon energies, or coincidence detection to probe correlation-driven effects with even higher resolution.

Our results also highlight the power of under-threshold attosecond interferometry as a uniquely sensitive probe of many-body correlations intrinsic to the ionization of atomic, molecular, or solid-state systems. In molecules, this approach can be used to investigate autoionization timescales, photoionization time delays between different vibrational levels of ionic states [36,37], effect of Feshbach resonances [38], shape resonances [39–42], etc., offering a route to disentangle channel-specific ionization delays with attosecond temporal and angular resolution [36,43–45]. It is expected that spectral congestion in the photoelectron spectra of molecules will make the extraction of phase information significantly more difficult; however, recent theoretical [46,47] and technical developments [48] and advanced detection schemes, such as photoelectron-photoion coincidence analysis with COLTRIMS approach, offer promising avenues for extending angle-resolved time-delay measurements into the molecular frame. In solid-state systems [49–54], Auger processes and excitonic resonances can be investigated through uRABBITT for time-domain analysis of band- and spin-dependent photoemission phases. Beyond spectroscopy, the strong spectral sensitivity of the uRABBITT suggests opportunities for coherent control of photoionization, where the optical parameters can be tuned to steer electron emission with attosecond precision.

By demonstrating simultaneous access to conventional and under-threshold RABBITT within a single system, and by harnessing the interplay between spin-orbit coupling and continuum-resonance interaction, our work opens a path toward a deeper understanding of electron dynamics at the attosecond timescale, bridging the gap between structure, correlation, and ultrafast coherence.

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DATA AVAILABILITY

The data that support the findings of this article are not publicly available. The data are available from the authors upon reasonable request.

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